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In This Issue

Page

Concerning the Division of High-Polymer Physics of the American Physical Society W. JAMES LYONS 729

Electrostatic Properties of Rubber and GR-S R. S. HAVENHILL, H. C. O'BRIEN, AND J. J. RANKIN 731

Speed of Retraction of Rubber R. B. STAMBAUGH, MARGARET ROHNER, AND S. D. GEHMAN 740

Some Relations Between Stress, Strain, and Temperature in a Pure-Gum Vulcanizate of GR-S Synthetic Rubber FRANK L. ROTH AND LAWRENCE A. WOOD 749

Limiting Law of the Reinforcement of Rubber HUGH M. SMALLWOOD 758

Some Low Temperature Properties of Elastomers F. S. CONANT AND J. W. LISKA 767

Frank B. Jewett Fellowships in the Physical Sciences 779

Contributed Original Research

Stress-Temperature Relations in a Pure-Gum Vulcanizate of Natural Rubber LAWRENCE A. WOOD AND FRANK L. ROTH 781

In Every Issue

Calendar of Meetings 778

Here and There 780

Recent Applications of Physics 790

Index to Advertisers xxvi

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Concerning the Division of High-Polymer Physics of the American Physical Society

BY W. JAMES LYONS

Secretary, Division of High-Polymer Physics

DURING recent years there has occurred an expanding recognition on the part of research directors and scientists of the unique efficacy of physical principles and techniques in the study of such materials as rubbers, textiles, and plastics. Concomitantly, the physicists engaged in research on these high-polymeric materials have perceived a need for an organization which would provide improved opportunities for the exchange of information and ideas contributory to the attack on problems in the field of high-polymer physics. This need was brought into rather sharp focus when, with the entry of the United States into World War II, our supply of natural rubber was abruptly halted, and America turned to the large scale production of synthetic rubbers—new and relatively unfamiliar materials. Under the impact of wartime urgency, physicists in the rubber research laboratories of the country were called upon to accelerate their studies of the properties and fundamental behavior of synthetic rubbers, and to extend their research techniques to the newer types and formulations being produced. With the specialized field developing faster than text and reference books could be written and published, it became apparent that it was only to personal discussion with his colleagues that the research worker could turn for inspiration. Similar developments, though perhaps not quite so rapid, had occurred over the span of recent years in physical research on textiles, plastics, and pulp and paper also.

It was logical that the physicists engaged in high-polymeric research should consider the formation of a division in the American Physical Society to fulfill their needs. Petitions to the Council of the Society, for the establishment of a division to be devoted to the physics of high-polymeric materials, were circulated during the fall of 1943. These activities culminated in a meeting held, under the chairmanship of Dr. Warren F. Busse and at the invitation of Society officers, at Evanston, Illinois, on November 12, 1943. That same day the Council, responding to the petitions, which had been signed by thirty-one Fellows and Members of the Society, and to formal oral request

High-Polymer Physics

Originally, it was expected that all of the papers from the inaugural meeting of the Division of High-Polymer Physics of the American Physical Society would be published in this issue. Unfortunately, because of WPB restrictions on the use of paper, this has not been possible and only five papers from this meeting are included. Since all of the space in the December issue was already allotted, it is expected that the remainder of the available papers on high-polymer physics will be published in the January, 1945 issue.

The Editor

made at the meeting, authorized a Division of High-Polymer Physics. Thus, within one year a second division of the Society had been launched, the Division of Electron and Ion Optics* having been authorized on May 1, 1943.

An Organizing Committee consisting of Council representatives (headed by Dr. K. K. Darrow as Chairman), and members of the Society sponsoring the new Division (led by Dr. J. H. Dillon), was subsequently appointed by the President of the Society. The Committee went to work immediately on the precise formulation of the objectives of the Division, on drawing up by-laws, and making plans for the first meeting. Over 250 original members were enrolled in the Division by April 20, 1944. While the Division had had potential existence since its authorization, it was formally established at an Inaugural Meeting held conjointly with that of the Society at Rochester, New York, on June 23 and 24, 1944. This meeting, with its scientific program of twenty-two papers on physical research on rubbers, plastics, textiles, and high polymers in general, was (conservatively speaking) a marked success. Working in cooperation with the temporary officers of the Division and the speakers on the inaugural program, the *Journal of Applied Physics* in the present issue publishes the first of these papers.

The formal statement of the object of the Division, as incorporated in the by-laws, declares that object to be "the advancement and diffusion of the knowledge of the physics of high-polymeric materials of any kind. Illustrative examples include rubbers, textiles, plastics, pulp and paper, paints and varnish, leather." The scope of the Division is envisioned as being sufficiently broad to embrace alike the interests of those working in academic, industrial, and governmental laboratories, whether these interests be focused on the fundamental physics of high-polymer behavior, or on the problems arising from the application of these materials to use by society. It is intended, however, that precaution be exercised to maintain the interests of the Division at a high scientific level, consistent with its relationship to the American Physical Society. It may be expected that, as a result of the activities of this Division, high-polymer physics as a recognized body of knowledge will become more distinctly defined.

One of the issues which has been brought to the attention of the sponsors repeatedly since the inception of the Division is the matter of time to be allotted papers on divisional programs. In general the interested members tend to favor the shorter program with an ample period for the presentation of each paper, and the allowance of at least ten minutes for discussion. Recognizing this preference, the framers of the by-laws incorporated therein no restrictions on the time to be allotted either invited or contributed papers. The matter is left to the discretion of the Executive and Program Committees, who, it may be confidently expected, will be guided by whatever policy is currently favored by the membership.

Meetings of the Division may be held conjointly with or separately from meetings of the Society. The titles and abstracts of papers presented at meetings held with the Society will be published in the *Bulletin* and subsequently in *The Physical Review*. When and if feasible, programs of divisional meetings held separately will be similarly published. The Division has adopted no official organ of publication, though the *Journal of Applied Physics* has been designated in the by-laws as the medium for official announcements. It is expected that a large number of the papers presented on divisional programs will be published in full in this journal. Some papers will be found to be more appropriate for *The Journal of Chemical Physics* or *The Review of Scientific Instruments*.

Any Fellow or Member of the American Physical Society may enroll in the Division of High-Polymer Physics. No restriction is placed on members of this Division against their joining any other division of the Society. For those scientists and research workers who are not members of the Society, but who are interested and qualified in high-polymer physics, the Division provides an associateship. Associates of the Division will receive announcements of, and may participate in, the activities of the Division, lacking only the rights to vote and to hold office.

* J. R. Pierce, J. App. Phys. **15**, 517 (1944).

Electrostatic Properties of Rubber and GR-S*

BY R. S. HAVENHILL, H. C. O'BRIEN, AND J. J. RANKIN

Research Laboratories, St. Joseph Lead Company, Josephtown, Pennsylvania

(Received July 5, 1944)

A new "electrostatic modulator" for measuring the electrostatic charges on various materials is described in this paper. In this apparatus the electrostatic lines of force established between the charged specimen and the grid of an audiofrequency amplifier are cut or modulated at audiofrequency by a motor-driven fan. The resultant alternating current voltage is amplified and measured on a meter in the output circuit. This device, in conjunction with a mirror surfaced metal plunger system for contacting the sample, has been used to measure the contact potential of various rubber and GR-S compounds. Data are shown on both rubber and GR-S compounds, and they bear out the formulation of an "electrostatic contact potential theory of reinforcement" in which reinforcement is explained on the basis of contact potentials and resultant electrostatic forces set up between the rubber and the reinforcing agents. By the application of this theory, organic materials, which have a highly positive charge, such as polymerized Trimethyldihydroquinoline and Flectol H, have been found to increase the tensile of GR-S pure gum type compounds as much as fivefold and to nearly double the tensile of high zinc oxide GR-S compounds.

CAREFUL observations on the triboelectrification of rubber, by a number of investigators[1–10] in the past, have disclosed many discrepancies and anomalies. A large number of these can be traced back to inadequate measuring devices, and also to the fact that the surface charge or contact potential on rubber does not spread uniformly over the surface but is usually spotty because of surface irregularities and incomplete contact with the other contacting member.

As is well known, when two dissimilar materials are rubbed or pressed together and then separated, equal and opposite charges are produced on the two materials. The amount of charge as well as the sign is dependent on the nature of the contacting surfaces.[12] By pressing various materials together, separating, and then measuring the magnitude and sign of the charge, a triboelectric or contact potential series[1,2,4] can be arranged. Rubber is at the negative end of the list while certain complex resinous organic materials are at the most positive end of the series. Since like charges are known to repel while unlike charges are known to attract, we might expect that if a highly positive material is milled into rubber, which is itself very negative, that a very strong electrostatic bond would result and might give rise to reinforcement of the rubber. In fact, the tensile strength of pure gum GR-S stocks which have a normal tensile strength of 14 kg/cm² has been increased to 77 kg/cm² while the tensiles of high zinc compounds have been increased from 70 kg/cm² to 121 kg/cm² by the addition of highly positive organic compounds.

It is the purpose of this paper to describe a new electrostatic modulator which is used in conjunction with a standard audio amplifier and output meter to measure the contact potentials of rubber and GR-S both compounded and uncompounded and also certain compounding ingredients; and to point out further that there is apparently a partial correlation between the electrostatic behavior of these materials and the reinforcement of both rubber and GR-S.

VACUUM-TUBE VOLTMETER

To overcome the disadvantages of the gold leaf electroscope, which are well known, attempts have been made to utilize the high gain of vacuum tubes. These devices are fine for indicating the sign of the charge, but they are of little value for measuring the magnitude of an electrostatic charge. For example, when a sample of crude rubber, having a clean, smooth, and uncharged surface, is brought into intimate contact with a similar sample of GR-S, electronic rearrangement takes place, and when the samples are separated the GR-S will have a negative charge and the rubber will have a positive charge. In other words, the GR-S will rob the rubber of a certain number of electrons, making

* Presented on June 23, 1944 before the Inaugural Meeting of the Division of High-Polymer Physics of the American Physical Society at Rochester, New York.

it negative, and the loss of these electrons will in turn leave the rubber positive.

The sign of the charge can be determined by holding the contacted and charged surfaces of the samples up to a 7.5-cm diameter metal plate attached to the free grid of a V.T.V.M. such as the one shown in Figs. 1 and 2. When the rubber

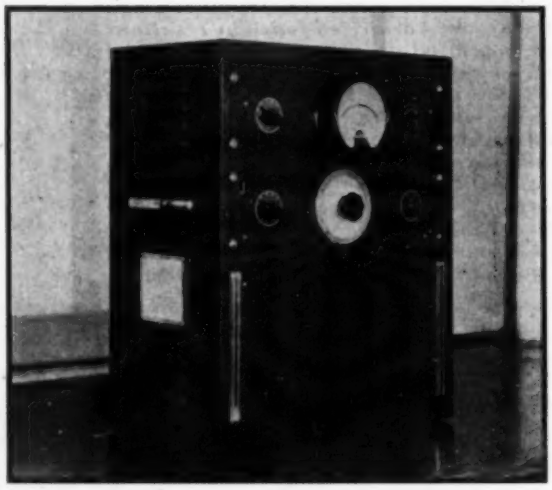

FIG. 1. Vacuum-tube voltmeter.

sample is brought up to the grid plate the meter needle moves to the right indicating a positive charge. When the GR-S sample is brought up to the grid plate, the meter needle moves to the left indicating a negative charge.

The samples can be de-ionized (decharged) prior to contact with each other by exposing them to an open flame. When completely de-ionized, they should produce no deflection of the V.T.V.M. when brought up close to the grid plate.

These same experiments can be repeated with disks (4-cm diameter) of cured stocks died out from tensile sheets cured in chromium-plated molds. In this case also, the rubber will be positive to the GR-S.

While the sign of the charge can be determined with this instrument, the magnitude cannot be measured, as the needle will soon return to zero because of leakage in the grid circuit, even though the charged rubber sample has not been moved relative to the grid plate and is still charged.

VIBRATING GRID TYPE INSTRUMENTS

Early in our electrostatic work we discovered that when the meter reading started to drop it could be maintained either by moving the charged sample closer to the grid plate or by moving the grid plate closer to the sample. This led to experiments with a device in which the sample was mounted on the face plate of a lathe and a small high speed grinder positioned on the power-driven cross feed so that the sample could be buffed accurately. The grid plate, which was connected to the grid of an audio amplifier, was mounted on the lathe bed about 0.5 cm from the rubber test specimen so as to pick up the charge developed by buffing or the contact potential between buffing wheel and sample. This apparatus was only fairly satisfactory. A photograph of this apparatus is shown in Fig. 3. The grid plate pick-up is not shown, as this set-up is used only for precision buffing of the samples prior to regular contact potential tests.

To obtain a steady meter reading and also do away with the necessity of a high gain direct coupled d.c. amplifier, the vibrating grid type electrostatic voltmeter[7, 8] has been developed which utilizes a high gain a.c. amplifier. In this device the capacity between the charged sample and the vibrating grid plate, which is connected to the grid of the a.c. amplifier, is continually changing at audiofrequency so that the original electrostatic potential or charge on the specimen

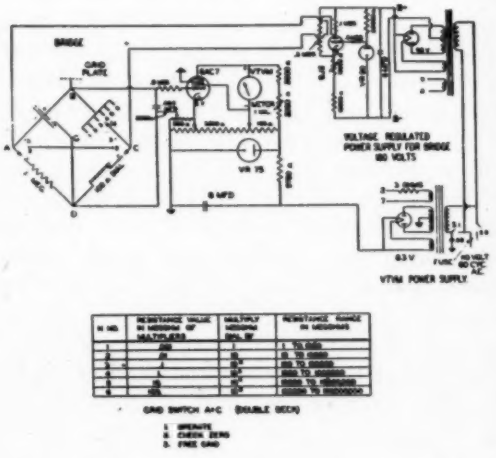

FIG. 2. Schematic wiring diagram of vacuum-tube voltmeter and megohm bridge.

is changed in effect into an alternating voltage which is easily amplified by the high gain a.c. amplifier. In this apparatus it is difficult to control the amplitude of the vibration to narrow limits, and any change caused by damping of the

apparatus and resonance greatly affects the accuracy of measurement. Adequate shielding of the vibrator and grid circuits is also difficult.

ELECTROSTATIC MODULATOR

In our new electrostatic modulator, the electrostatic lines of force between the charged specimen and the stationary grid plate are cut at audiofrequency (300 cycles per second) by a small motor-driven four-bladed fan. This produces in effect an alternating current voltage of approximately sine wave to the audio amplifier. The output can be connected to a speaker and heard as a hum, observed on the cathode-ray oscillograph, or, preferably, it can be observed on a regular output meter so that accurate quantitative data can be obtained. The greater the charge on the sample the stronger the resulting electrostatic field and the greater the amplitude of the resulting voltage furnished to the a.c. amplifier. Extremely minute charges can be measured with this device such as the charge put on a sample of rubber by merely touching it, and the charge on a Lucite rod can be detected at a distance of 10 or 15 feet. The range and sensitivity of the instrument can be varied by the distance of sample from grid plate and by the gain controls on the amplifier. Since the grid plate is stationary, the apparatus does not suffer from resonance and shielding difficulties.

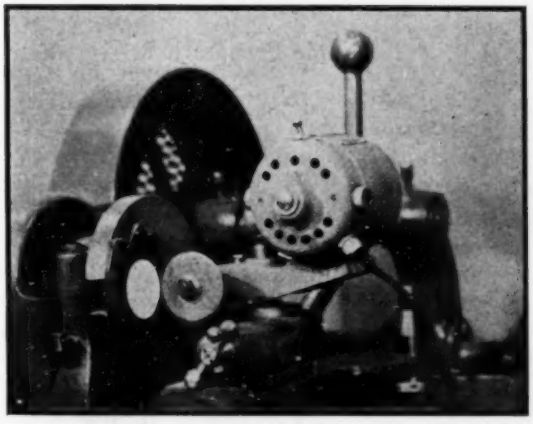

FIG. 3. Lathe buffing set-up.

A photograph and line drawing of the electrostatic modulator are shown in Figs. 4 and 5.

This unit can be plugged into the microphone input of an ordinary public address system and electrostatic charges can be heard as a hum in the loudspeaker when the charged sample is brought near the charge plate or the charge plate can be replaced by a cup and the charged sample dropped into the cup.

CONTACT POTENTIAL APPARATUS

Our apparatus for measuring the contact potential of rubber sheets is shown in the photograph—Fig. 6—and the line drawing—Fig. 7.

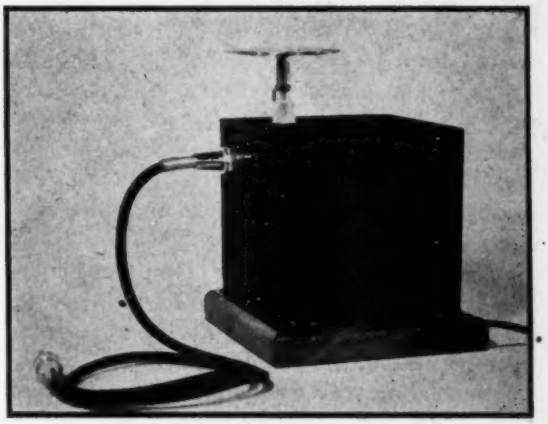

FIG. 4. Electrostatic modulator.

It will be noted that it consists of four main parts.

I. The metal specimen holder which is mounted on a Lucite or polystyrene insulator.

II. The mirror surfaced steel plunger which contacts the sample and acts as the reference surface against which the contact potential is measured. Lucite or polystyrene insulation is used to insulate completely the plunger. Means are provided to press the plunger down against the rubber test specimen, with a constant force provided by the primary and secondary springs. Quick release of the plunger from the test specimen is obtained by the use of the stiff springs and the latch at the top of the sliding plunger shaft. The average velocity of the plunger is 225 cm per second. The spring exerts a pressure of 1.58 kg/cm^2 on the test specimen which is a disk 4.13 cm in diameter and 0.19 cm in thickness. The specimen is held in place by the ring and thumb nuts. Occasional arcing was detected between the charged sample and the holder ring and also in some cases the test specimen partially stuck to the plunger and was pulled slightly away from the sample holder. When this occurred a plus charge was, of course, put on the sample holder and this neutralized the negative charge already on it and gave an abnormally low contact

potential reading. To eliminate this trouble, a smaller disk, 2.54-cm diameter, was used, and it was cemented into the holder with Vulcalock cement. The presence of the cement did not alter the contact potentials. The plunger pressure on the smaller sample was 2.5 kg/cm².

Quick release of the plunger is very important, as the quicker the release the higher the contact resistance and the less chance of electrical leakage, which would lower the contact potentials.

III. The electrostatic modulator is built into this apparatus. The charged sample charges the sample holder and electrostatic lines of force are set up between the charge plate and the grid plate. The fan cuts these lines of force or modulates them at audiofrequency, which in effect produces an a.c. wave which is amplified by the audio amplifier.

IV. The audio amplifier schematic is shown in Fig. 8. While any good audio amplifier such as one used in commercial public address systems will be suitable, the amplifier used was made in our own laboratory and designed especially for this use. The grid bias for the 6J7 input stage is supplied by a one-volt bias cell, and the input resistance which is ordinarily around 5 megohms has been removed to give a better impedance match to the modulator unit. The input stage must be completely shielded. The 6N7, which is a dual-triode tube, is used as a phase inverter and second audio. The grid circuit of this second audio is provided with a selector switch so that various values of grid resistances can be switched in so as to take care of a wide range of input voltages and still obtain nearly full scale deflection on the output meter for all ranges.

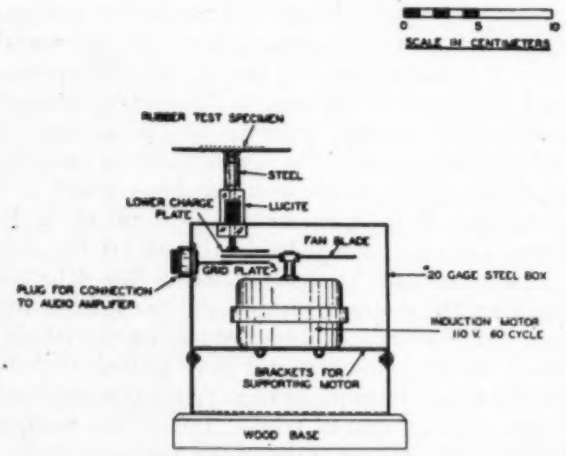

FIG. 5. Electrostatic modulator.

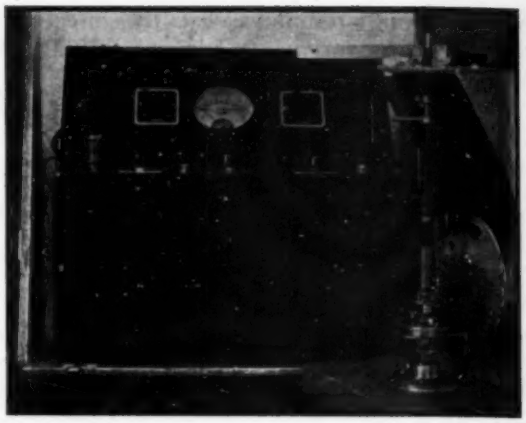

FIG. 6. Electrostatic contact potential apparatus.

The output stage consists of two 6L6 beam power tubes which operate in push-pull.

Instead of using the customary copper oxide rectifier in the output meter, a tube rectifier was used.

The amplifier was made to have a linear response so that the output meter readings would be directly proportional to the input voltages and electrostatic charges on the test specimens. Calibration was obtained by the use of an audio oscillator and vacuum-tube voltmeter.

This amplifier has a gain of 110 db and a power output of 20 watts.

EXPERIMENTAL PROCEDURE

Sample Preparation

Before contact potentials can be obtained on rubber samples the specimens must have a clean, smooth, uncharged surface. This is very difficult to obtain, as, if anything is used to clean the surface such as a clean cloth and solvent, a contact potential will be set up between the cloth and specimen and also between the solvent and specimen. The solvent also may make the surface of the specimen more mobile so that electrostatic rearrangement may take place more easily, resulting in greater contact potentials. The cloth may leave particles of lint on the surface which will charge up and which may also serve as focal points for point discharges of the charge on the specimen itself. When the sample is picked up from the table or, in fact, if it is in contact with any material, electrostatic charges will be set up when the sample is moved. This makes it extremely difficult to obtain suitable specimens for testing. In addition to dust, lint,

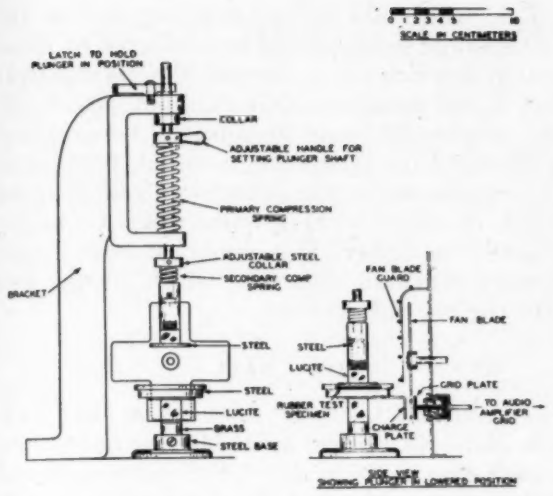

FIG. 7. Electrostatic contact potential apparatus.

and other foreign matter which may contaminate the surface, certain compounding ingredients such as sulfur, accelerators, stearic acid, etc., may bloom to the surface and alter completely the contact potential. There is also the possibility of skin effects and pigment segregation which may cause trouble. One method of overcoming these difficulties is to use buffed samples as suggested by Liska.[10] Our lathe set-up for precision buffing is shown in Fig. 3.

While fairly good data have been obtained using buffed specimens, especially on carbon black stocks where it is usually essential, buffing has one serious disadvantage. It produces a rough surface of unknown and variable surface area for testing.

Fairly good results have been obtained by curing the samples in clean, chromium-plated molds. However, care must be taken to avoid touching the samples, and they must be kept between Holland (linen sheets) in a desiccator. In addition, the samples must be tested shortly after cure before blooming has a chance to occur.

In some cases it is, of course, necessary to clean the surface with freshly distilled acetone or ether with a clean, lint-free cloth. If a slight excess of acetone is used the sample will usually remain uncharged. Benzol or alcohol should not be used as the samples may be difficult to charge because of difficulty in removing the last traces of residual solvent, which may contain moisture. It is necessary in some cases to decharge the sample with a free flame. Acetone should not be used on uncured rubber or Buna S specimens as it softens the polymer so that a clean separation between plunger and polymer cannot be made. This sticking of part of the sample to the plunger gives low contact potential results.

TESTING PROCEDURE

A 2.54-cm diameter disk is died out from a tensile sheet which is 0.19 cm thick and the specially prepared or buffed sample is cemented in the sample holder with Vulcalock cement. The plunger and sample holder are discharged by momentarily touching with a grounded wire. The plunger is brought into contact with the test specimen by pushing down on the plunger handle until the latch can be swung over the top end of the plunger shaft holding it in place. The metal plunger is now touched with the ground wire and if the sample is not properly prepared and has an initial charge, prior to placing it in the holder, a reading will be observed on the output meter. The specimen holder is then discharged by momentarily touching it with the ground wire. This, of course, brings the meter reading back to zero. After the plunger has been in intimate contact with the sample for 15 seconds and the plunger and sample holder have again been touched with the ground wire, the latch is released and the plunger quickly rises and breaks contact with the sample. The plunger

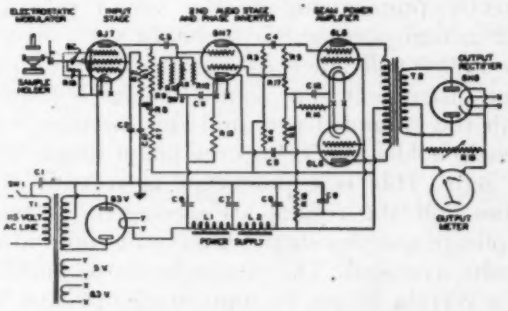

FIG. 8. Schematic wiring diagram of the audio amplifier.

Circuit constants of audio amplifier.

$C_{1,2,3,4,5}$ = 0.1 μf 600 v d.c.
$C_{6,7,8,9,10}$ = 8 μf 600 v d.c.
$C_{11,12}$ = 50 μf 50 v d.c.
$L_{1,2}$ = 30 henry 150-ma choke coil.
R_1 = 200 M ohms 1*W*.
R_2 = 1 megohm 1*W*.
$R_{3,4}$ = 100 M ohms 1*W*.
$R_{5,6}$ = 500 M ohms 1*W*.
$R_{7,8}$ = 25 M ohms 1*W*.
R_9 = 100 ohms 1*W*.
R_{10} = 500 ohms 1*W*.
R_{11} = 1000 ohms 1*W*.
R_{12} = 500 M ohms 1*W*.
R_{13} = 3000 ohms 5*W*.
R_{14} = 200 ohms 20*W*.
R_{15} = 60 ohms 10*W*.
R_{16} = 25 M ohms 50*W*.
R_{17} = 15 M ohms .1*W*.
R_{18} = 5 megohms 0.5*W*.
T_1 = Power transformer input 115 v a.c. Output—350–0–350, 5, 6.3 v a.c.
T_2 = Output transformer 6L6 p.p. to 30 ohms.
SW_1 = power switch for 110 v a.c.
SW_2 = 4-tap switch, rotary, well insulated.
Output meter = 0–1 milliampere.
B. C. = 1 volt bias cell.

charge is + while that on the rubber is negative. This can easily be checked by a proof plane and V.T.V.M. In fact, all of the stocks tested to date have shown a negative charge relative to the mirror surfaced metal plunger. The plunger is

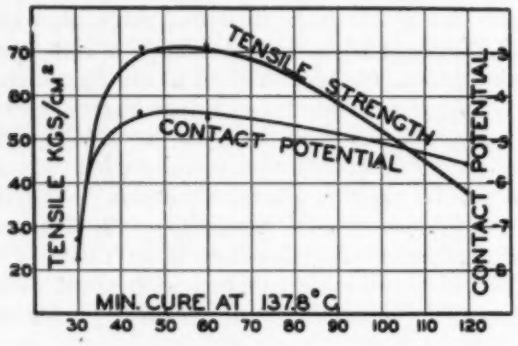

FIG. 9. Rate of cure and electrostatic contact potential curves.

then discharged or brought to ground potential by touching it with the ground wire which immediately produces an additional increase in meter reading because of the absorption of electrons from the ground by the plunger. This final steady meter reading is recorded as the contact potential. While this reading is, of course, not the actual potential on the sample, it is nevertheless directly proportional to the actual potential. The actual potential is probably very high, in the 10,000-volt range, as indicated by the Braun type instrument. The sample holder is touched with the grounded wire and this discharges the sample holder and brings the meter needle back to zero. This test procedure is repeated five times and the results are averaged. Tests on duplicate samples should always be run and the results averaged. The charge tends to build up to a certain extent in some stocks so that the latter readings are somewhat higher than the initial ones.

All tests should be conducted in a constant temperature, constant humidity room maintained at 78°F, and not over 50 percent relative humidity. High humidity causes erratic results in electrostatic work just as it does in resistivity, dielectric constant, and power factor tests, only to a greater extent.

EXPERIMENTAL DATA

As has been previously intimated, our electrostatic contact potential theory of reinforcement is based on the assumption that rubber and GR-S, which are at the negative end of the electrostatic series, should be reinforced by those materials which are on the positive (less negative) end of the series and that the more positive or the greater difference in potential between the rubber and the reinforcing material, the greater the reinforcement. The converse should also hold true if materials could be found which are highly negative to rubber. This would establish a high contact potential difference which should also give rise to reinforcement.

GR-S DATA

To test out this theory, one of the most positive materials we had available was milled into a high zinc oxide loaded GR-S compound and the stock tested for tensile and contact potential. From the results of a previous electrostatic investigation polymerized Trimethyldihydroquinoline, an organic resin, was found to be one of the most positive materials and fifteen parts of it were milled into the stock. A control was also run in which the organic resin was omitted. The tensile results indicated that a 75 percent increase in tensile strength and an acceleration in cure were obtained by the use of this positive material and the electrostatic contact potential data showed that the stock was highly positive (less negative) than before it was added. These preliminary results confirmed our theory. Further experiments were then carried out in a carbon black stock, a pure gum stock, and another zinc oxide stock. The zinc oxide used in this and all subsequent tests was a fine particle size (0.2-micron average diameter), fast curing type produced by the St. Joe electrothermic process. The results are shown in Table I, and indicate a definite relationship between tensile and contact potential. For these and all subsequent tests Flectol H, an acetone-aniline condensation product, which is also a highly positive resin and is easy to incorporate in rubber, was used. Previous investigators in electrostatics[4,10] have stressed the importance of dielectric constant, power factor, and resistivity data; these, along with some other physical tests, are included.

DIELECTRIC CONSTANT AND POWER FACTOR TESTS

These data were obtained on a series resistance bridge with Wagner ground, using a 1000-cycle oscillator and three-stage electronic eye null indicator. Refer to A.S.T.M. D150-42T.

TABLE I. Electrostatic contact potentials of GR-S compounds.

Formula No.	Composition	Optimum cure	*Electrostatic contact Potential	Tensile kg/sq. cm	Elong. %	Mod. @ 400% kg/sq. cm	% Rebound 25.6°C	% Rebound 100°C	Dielectric constant	% Power Factor	D.c. resistivity Ohm cm	Shore hardness 30 sec.
A	Tread with (+resin)	75′ @ 145°C	−1.3	203.9	700	75.6	26.3	31.8	8.6	17	2.4×10^{10}	47
	Tread	90′ @ 145°C	−2.1	196.9	525	137.1	31.8	38.1	34.6	73	8.9×10^{7}	50
B	ZnO with (+resin)	15′ @ 137.8°C	−4.0	121.3	800	19.3	32.0	42.8	4.4	1.15	1.6×10^{14}	41
	High ZnO	45′ @ 137.8°C	−5.0	70.3	1050	7.0	35.1	35.7	4.3	.43	2.8×10^{14}	31
C	Pure gum with (+resin)	10′ @ 137.8°C	−6.0	31.6	600	17.6	38.5	48.0	2.75	1.20	1.7×10^{14}	32
	Pure gum	25′ @ 137.8°C	−8.0	14.1	725	3.5	43.1	42.2	2.60	.32	2.0×10^{14}	25

Formulae

A		B		C	
GR-S	100	GR-S	100	GR-S	100
E.P. carbon black	50	Sulfur	2.5	Sulfur	2.5
Sulfur	1.5	Captax	1.5	Captax	1.5
Captax	1.5	ZnO	5.0	ZnO	5.0
Bardol	5.0	Stearic acid	2.5	Stearic acid	2.5
ZnO	5.0	ZnO	113.0	Positive resin	0 —15
Positive resin	0 —15	Positive resin	0 —15		111.5
	163.0		224.5		

*For all tables and graphs the electrostatic contact potential readings divided by 10 equals the actual input volts to the amplifier.

RESISTIVITY DATA

The resistivity tests were run on the St. Joe megohm bridge, using Aquadag electrodes, as suggested by Liska.[10] A photograph and schematic diagram of the St. Joe megohm bridge with built-in vacuum-tube null indicator and 180-volt d.c. voltage regulated power supply are shown in Figs. 1 and 2.

It will be observed on examination of the data in Table I that there are notable exceptions to Coehn's[4] rule, which states that the charge is a function of the dielectric constant and that a material is positive to another if it has a higher dielectric constant. There also appears to be no definite relationship between resistivity and contact potential.

Rebound data were obtained using the St. Joe inclined plane falling ball rebound tester.[11] The results indicate that while the *positive resin* decreases the rebound at room temperature, it actually increases it above the regular compound in some cases at 100°C.

EFFECT OF VULCANIZATION OF GR-S ON CONTACT POTENTIAL

The effect of vulcanization on contact potential and tensile strength is shown in Table II and Fig. 9. It will be noted that the cure curves and the contact potential curves are of a similar shape.

The results on GR-S indicate that while there is no definite relationship between dielectric constant, resistivity, and contact potential, there does appear to be some correlation of tensile strength or reinforcement and contact potential which checks our theory.

TABLE II. Effect of vulcanization on electrostatic contact potentials of GR-S stocks.

Cure minutes at 137.8°C	Electrostatic contact potential	Tensile strength kg/cm²	Elongation %	Modulus at 400% kg/cm²	Remarks
0	−9.0	Less than 14	—	—	Too soft to test
1	−8.5	Less than 14	—	—	Too soft to test
15	−8.0	Less than 14	—	—	Too soft to test
30	−7.4	22.9	1325	0.7	
45	−4.3	70.3	1075	5.9	
60	−4.5	70.3	950	10.6	
120	−5.5	35.2	550	19.3	

Formula	Parts by weight
GR-S	100
Sulfur	2.5
Captax	1.5
ZnO	5.0
Stearic acid	2.5
ZnO	113.0 (20 volumes)
	224.5

DATA ON RUBBER COMPOUNDS

If the theory is any good, the highly *positive resin* should also increase the tensile strength of not only GR-S stocks but also rubber compounds, and these data are shown in Table III.

TABLE III. Electrostatic contact potentials of rubber compounds.

Formula No.	Composition	Optimum cure Min. @ 134.4°C	Electrostatic contact Potential	Tensile kg/sq. cm	Elong. %	Mod. @ 400%	% Rebound 25.6°C	% Rebound 100°C	Dielectric constant	% Power Factor	D.c. resistivity ohm cm	Shore hardness 30 sec.
D	Tread with (+resin)	60	−1.0	288.3	638	143.4	26	33.1	9.4	16.7	7.0×10^{10}	63
D	Tread	60	−1.5	283.7	575	175.8	30.3	42.9	34.6	71.1	7.1×10^{7}	55
E	20 Vol ZnO with (+resin)	20	−2.0	283.0	678	90.4	41.4	58.3	3.94	.53	3.6×10^{14}	49
F	Gum with (+resin)	40	−2.5	277.7	717	43.9	45.3	65.3	2.80	.51	3.3×10^{14}	43
E	20 Vol ZnO	40	−4.7	244.3	657	73.8	46.2	57.1	4.06	.46	4.9×10^{14}	46
F	Pure gum	60	−6.0	233.8	850	22.9	51.4	61.5	2.70	.32	6.0×10^{14}	37

Formulae

D		*E*		*F*	
Rubber	100	Rubber	100	Rubber	100
Sulfur	2.7	Sulfur	3.5	Sulfur	3.5
Captax	0.9	Captax	0.6	Captax	0.6
Zinc oxide	3.0	Stearic acid	2.0	Stearic acid	1.5
Stearic acid	4.0	ZnO B No. 20	113.0 (20 vol.)	ZnO B No. 20	5.0
Pine tar	2.0	Positive resin	0.0— 15	Positive resin	0.0— 15
B.L.E.	1.5		219.1—234.1		110.6—125.6
E.P. carbon black	52.0				
Positive resin	0.0— 15.0				
	166.1—181.1				

The fact that the carbon black stock is not reinforced by the positive resin would be expected, as it does not make the contact potential appreciably more positive; and furthermore, the carbon black charge is probably in the same potential range, while in the rubber, as the resin charge.

HIGH TENSILE PURE GUM TYPE GR-S STOCKS

Since high gum type GR-S stocks have not as yet been produced, it was thought that if a large amount of the positive resin were added to the gum stock, high tensile stocks should result. Table IV gives the electrostatic contact potential and tensile data on a stock containing 30 parts of the positive resin. It will be noted that the resin has made the stock more positive (less negative) and has increased the tensile strength from 14 kg per square cm to 77 kg per square cm.

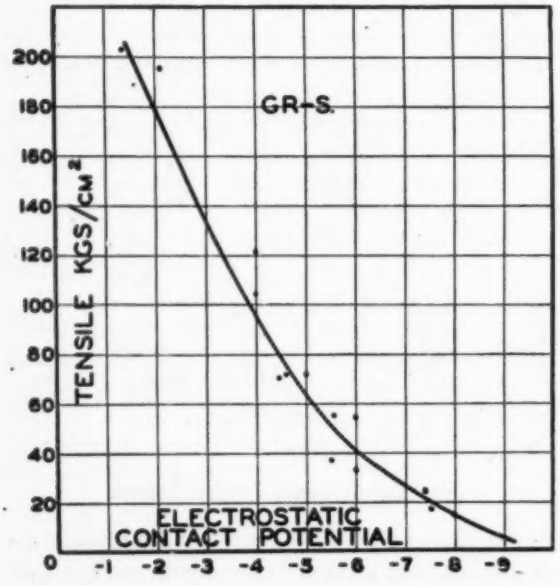

FIG. 10. Contact potential against tensile strength for all GR-S compounds.

APPLICATION OF THEORY TO PIGMENTS IN GR-S

While we have been unable to measure the contact potential of pigments such as carbon black and zinc oxide, if the theory is correct, we would expect these materials, when added to rubber, to produce a stock having a more positive (less negative charge). By checking over the results already given for GR-S and rubber on carbon black and zinc oxide stocks, Tables I to II!, it will be observed that the theory holds good even for pigments. As a further check, the results on several other stocks containing various pigments are shown in Table V. These data on clay, whiting, and Blanc Fixe again indicate the relationship between contact potential and reinforcement.

In Fig. 10 all of the contact potential data on GR-S have been plotted against the tensile strength of the resulting compounds and it appears that there is a relationship between tensile and contact potential.

In Fig. 11 all of the contact potential data on rubber have been plotted against the tensile strength of the resulting compounds and here

TABLE IV. High tensile pure gum type GR-S compound.

Cure minutes @ 137.8°C	30 parts of (+resin) added Formula *G* Tensile kg/cm²	% Elong.	Mod. @ 400% kg/cm²	No (+resin) added Formula *H* Tensile kg/cm²	% Elong.	Mod. @ 400% kg/cm²
10	75.3	705	21.1	7.0	700	0.7
15	77.3	700	21.1	14.1	650	3.5
25	65.2	450	33.4	14.1	425	5.3
40	57.5	425	32.5	13.0	300	6.7

	Formula *G*	Formula *H*
Electrostatic contact Potential cure 15′×280°F	−4.5	−8.0

Formulae	*G*	*H*
GR-S	100	100
Sulfur	2.5	2.5
Captax	1.5	1.5
Zinc oxide	5.0	5.0
Stearic acid	2.5	2.5
(+Resin)	30.0	0.0
	141.5	111.5

again there appears to be a relationship. However, it is a different one from that of GR-S as might be expected from the difference in physical and chemical properties of the two materials. The fact that the rubber is positive to GR-S accounts only partly for the higher tensile strength of the rubber compounds, while the fact that the GR-S is negative to rubber accounts in part for its lower tensile and also for the fact that it can be reinforced a greater percentage than rubber by the same materials which reinforce rubber.

SUMMARY AND CONCLUSIONS

A new electrostatic modulator has been described for measuring the electrostatic charges on rubber, synthetic rubber, and various materials. In this apparatus the electrostatic lines of force established between the charged specimen and

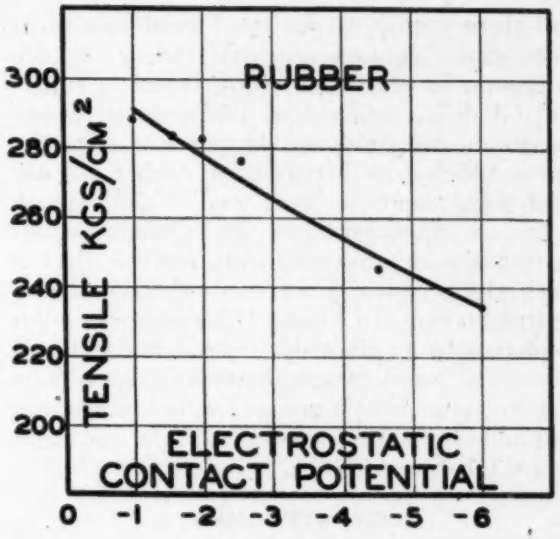

FIG. 11. Contact potential against tensile strength for all rubber compounds.

a stationary electrode plate connected to the grid of an audiofrequency amplifier are cut or modulated at audiofrequency by a small four-bladed, motor-driven fan. This produces in effect an alternating current voltage which can be readily amplified by the audio amplifier and quantitatively measured on a meter in the output circuit.

This device, in conjunction with a mirror-surfaced metal plunger system for contacting the rubber samples, has been used to measure the contact potential of various rubber and GR-S compounds.

Electrostatic contact potential data are shown for both rubber and GR-S compounds with and without organic and inorganic reinforcing agents,

TABLE V. Effect of various pigments in GR-S compounds on the electrostatic contact potential.

Pigment	Optimum cure Min. @ 145°C	Electrostatic contact Potential	Tensile kg/cm²	Elong. %	Mod. @ 400% kg/cm²	% Rebound 25.6°C	Dielectric constant *K*	% Power Factor	D.c. resistivity ohm cm	Shore hardness 30 sec.
Suprex clay (hard clay)	60	−4.0	103.7	793	21.1	34.9	3.72	1.8	1.6×10^{14}	45
Blanc Fixe (p.p.t. $BaSO_4$)	20	−5.5	56.3	918	5.3	34.6	3.48	.29	1.6×10^{14}	36
Calcene (p.p.t. $CaCO_3$)	20	−6.0	55.0	675	19.3	32.9	3.25	.5	1.1×10^{14}	42
Whiting—dry ground $CaCO_3$	20	−7.5	17.6	1000	—	36.8	3.26	.29	1.6×10^{14}	29

Base formula	Parts by wt.
GR-S	100
Sulfur	2.5
Captax	1.5
ZnO	5.0
Stearic acid	2.5
Pigment added	30 volumes

Pigment added to base formula	
Suprex clay	78
Blanc Fixe	128
Calcene	81.3
Whiting	81.3

and these data bear out the formulation of an electrostatic contact potential theory of reinforcement in which the reinforcement of rubber and GR-S is explained on the basis of contact potentials and resultant electrostatic attractive forces which exist between the rubber and the reinforcing agents.

By the application of this theory, organic materials, which have a highly positive electrostatic charge, such as polymerized Trimethyldihydroquinoline and Flectol H, an acetone-aniline condensation product, have been found to increase the tensile strength of GR-S pure gum type compounds as much as fivefold and nearly to double the tensile strength of high zinc oxide loaded GR-S compounds.

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Speed of Retraction of Rubber*

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A method of measuring the speed of retraction of rubber is described which utilizes an electronic timing circuit with photo-cell input. The results include measurements of the speed of retraction of Hevea and synthetic rubbers as a function of elongation, temperature, carbon black loading, and cure. They are discussed both from the standpoint of the new information which they give in regard to rubber structure and high elasticity as well as their practical application to evaluate quality and cure. High speed photographs are included which are of interest in showing the manner in which rubber retracts.

INTRODUCTION

THE most characteristic property of rubber-like materials which distinguishes them from other substances is the speedy and forceful retraction which occurs when they are released after stretching. Compounders use the "snappy" feel of stocks to judge quality and cure. Practically nothing has been known about the actual velocities of rubber retractions which undoubtedly are related to the molecular structure, modulus, internal friction, temperature, and other variables. The problem of determining cure has been accentuated by the introduction of various types of synthetic rubber and vulcanizing systems so that there is a need for new means of evaluating state of cure.

A brief description of the electronic method used for measuring the velocity of free retraction of rubber has been published.[1] High speed photographs showing the wave front of the retracting rubber band were included. Mrowca, Dart, and Guth[2] have described a method of measuring the retraction velocity using a smoked drum and a stylus attached to the rubber strip. They also have published similar photographs.

A few experiments are described in the literature, the object of which was to correlate the

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modulus with the velocity of an impulse along a rubber strip. These papers are discussed by Whitby[3] and show that the speed of retraction was measured as early as 1872.

The velocity acquired by a retracting strip of rubber is quite high—in the order of 100 miles per hour or more—so that it has been difficult to measure or photograph the "snap" which takes place in a few thousandths of a second. The method described below permits such measurements to be made with facility and may give information of much value from both a theoretical and practical standpoint.

METHOD

A schematic diagram of the apparatus used for measuring speeds of retraction is given in Fig. 1. The rubber strip (16.5×1.9×0.2 cm) is held in a horizontal frame having one grip (No. 1) fixed and one (No. 2) which slides in a channel in the frame. A wire cable which may be wound up on a spool is fastened to the movable grip so that, by turning a crank, the test strip may be extended to any desired elongation, and held there by a ratchet. The grips are of the familiar eccentric roller type adapted for quick release.

The strip intercepts two narrow beams of light from the lamps which are directed at photo-cells *A* and *B*. The beams are 2.65 cm apart at the rubber strip. When the strip is released from grip No. 1, it retracts and permits light to fall on photo-cell *A*. The photo-cell current puts a negative charge on the grid of the 9001 tube so that its plate current is cut off. When this occurs, the grid of the 6J5GT tube becomes positive and the tube conducts a current which is limited by the cathode resistor. This current flows into the capacitor in the plate circuit of the 6J5 tube, so that it begins to acquire a charge. When the rubber strip has retracted sufficiently for light to fall on photo-cell *B*, however, the photoelectric current produced causes the 9001 tube to become conducting again which biases the 6J5 beyond plate current cut-off. The capacitor retains the charge it had accumulated which is dependent on the time the charging current was flowing. The voltage on it is measured by a vacuum-tube voltmeter which consists of an ordinary bridge circuit using a 6C8G twin triode and a microammeter. The voltmeter has two ranges, 0 to 5 volts and 0 to 15 volts. A conventional regulated power pack supplies the power. Electronic timing circuits of this general nature have been used previously for a variety of purposes.[4, 5]

Since a much higher charging voltage is used (150 volts) than is ever acquired by the condenser (15 volts), the voltage measured was found to be practically proportional to the time interval. Calibration of the circuit was carried out by accurately measuring the condenser capacity and the charging current. The voltage is the integral of the current with respect to the time divided by the capacity. The speed of the rubber strip equals the distance between the light beams, divided by the time. Figure 2 is a photograph of the apparatus.

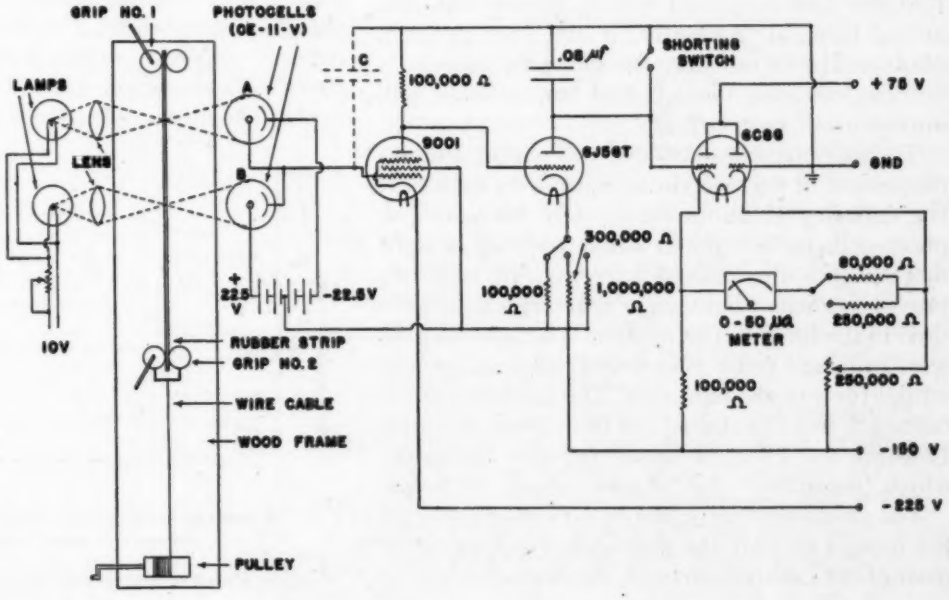

FIG. 1. Schematic diagram of apparatus.

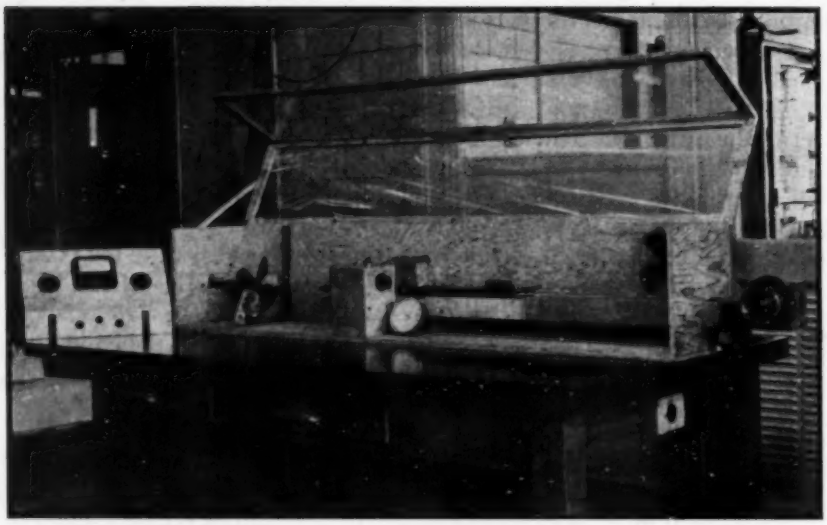

FIG. 2. Photograph of apparatus.

The design of the optical system and the photo-cell circuit is critical because of the short time intervals to be measured. The input capacity for the 9001 tube, plus the capacity of the photo-cells and wiring, must be as small as possible. This capacity is represented by the dotted condenser C in Fig. 1. When the light impinges on photo-cell A the current charges this capacity to about 22 volts negative. The current of photo-cell B then discharges the capacity and brings the voltage on the 9001 grid back to its original value. Thus it is obvious that if photo-cell A is not properly illuminated, it will take too long to start the charging action for the main 0.08-μf condenser so that the time measured will be shorter than the actual interval. Similarly, if the current from photo-cell B is too low, the charging current is not cut off soon enough and the velocity will appear lower than it really is.

To minimize these effects, the wiring and arrangement of parts in the housing were such that the capacity C amounted to only 9.5 $\mu\mu$f. The photo-cells each required about $\frac{1}{2}$ lumen of light flux to give the desired currents. In order to provide sufficient light, high aperture lenses were used in the illuminating system. The light sources were ordinary radio pilot bulbs, selected for the straightness of the filaments. The images of these filaments were projected on the rubber strip by 12.8-mm focal length lenses (10-mm diameter) which magnified the images about 3 times.

The photo-cells were placed far enough behind the images so that the flux spread out to cover most of the cathode surfaces. A microammeter in series with the photo-cells permitted the lamp brightness to be adjusted to the working range in case of bulb blackening, or replacement with a new lamp. The effect of photo-cell current on the accuracy of measurement is shown in Fig. 3. If the current is too small, the trigger action is so slow that it becomes an appreciable part of the time interval being measured, and thus the measurement gives too high a velocity. By maintaining the photo-cell current at a value of about 5 microamperes, this trouble was avoided for all velocities encountered.

A check on the calibration of the device was made by dropping a steel ball past the photo-cells. A wide tail was fastened to the ball to intercept the light beams. The ball was dropped from a height of 348 cm so that it had acquired a velocity of 827 cm/second when the measurement was made. The measured value was 828 ± 10 cm/sec.

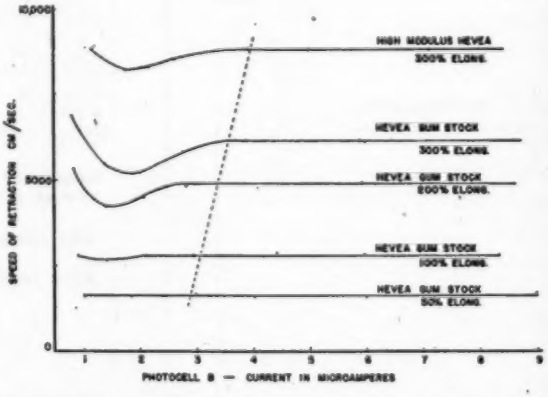

FIG. 3. Effect of photo-cell current on measurements.

The precision of the apparatus (that is, the consistency and reproducibility) is good, for there is very little scattering of points on the plots of the data, and measurements can be repeated to within about 5 percent.

The consistency of the readings obtained was further checked by placing a set of four small mirrors in the path of one of the light beams in such a way as to displace the beam parallel to itself. In this way the distance between the beams at the point at which they were intercepted by the test strip was varied from 1 to 5 cm. Using the same rubber strip at the same elongation, several different time intervals were measured for one velocity. This method extended the calibration to time intervals as low as 150 microseconds, which corresponds to a velocity of over 15,000 cm/sec. A typical calibration curve is shown in Fig. 4.

Probably the greatest source of variability is the permanent set and stress relaxation of the stocks, both of which would tend to reduce the velocity. To minimize these effects, the measurements were always made at low elongations first, proceeding to successively higher elongations. The length of the strip held in grip No. 1 was kept the same by always lining up the end of the strip with a mark on the grip. Grip No. 2 was reset after each measurement to correct for any slippage and permanent or temporary stretch.

If the rubber strip is released immediately after stretching to the desired elongation, stress relaxation is a minimum and the highest velocity is observed. If the strip is held in a stretched position for several seconds, an equilibrium condition is reached so that a lower velocity is obtained which is practically independent of the time before release. This is true only for stocks with low plastic flow. Butyl stocks, or even Hevea stocks

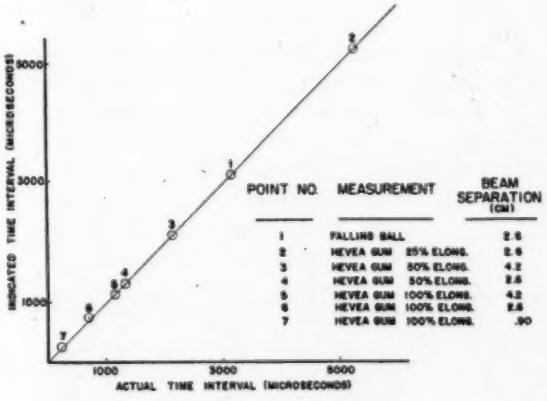
INDICATED TIME INTERVAL (MICROSECONDS)
ACTUAL TIME INTERVAL (MICROSECONDS)
POINT NO. MEASUREMENT BEAM SEPARATION (CM)
1 FALLING BALL 2.6
2 HEVEA GUM 25% ELONG. 2.6
3 HEVEA GUM 50% ELONG. 4.2
4 HEVEA GUM 50% ELONG. 2.6
5 HEVEA GUM 100% ELONG. 4.2
6 HEVEA GUM 100% ELONG. 2.6
7 HEVEA GUM 100% ELONG. .90

FIG. 4. Calibration curve.

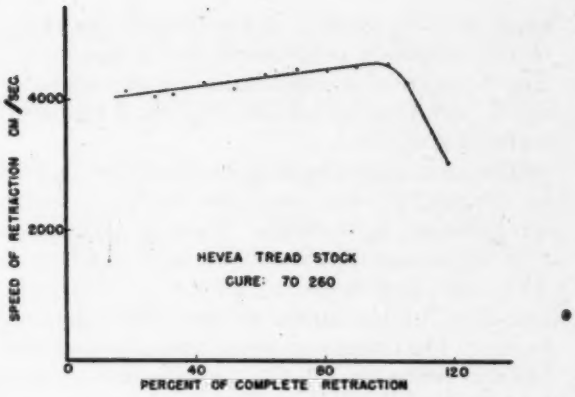

FIG. 5. Speed acquired during retraction.

which are undercured or very cold, will take longer to reach an equilibrium condition. However, for the purposes of comparison, a time interval of 30 seconds was consistently allowed for the strip to come to equilibrium.

For the sake of simplicity, all measurements were made when the moving end of the strip was 2 inches from grip No. 1. This corresponds to about 50 percent of full retraction at 100 percent original elongation, or 25 percent retraction in the case of 200 percent original elongation. A more refined system might include a mechanical linking of the photo-tube housing to the crank which extends the rubber strip so that the housing would be moved further from grip No. 1 at higher elongations, and all measurements would be made at the same percent of full retraction. However, it was not felt that the additional complications of such a system were worth while.

NATURE OF THE RETRACTION

A stretched strip of rubber which is suddenly released does not retract as a whole as a weighted spring would do. Instead the retraction occurs at the free end first and travels in a wave along the strip. In an ideal case, the wave would be reflected from the fixed end so that the strip would stretch out again. Actually, however, the energy of the retraction is dissipated by the inelastic impact at the grip and by the flopping of the retracted strip. Longitudinal wave transmission in bars has been analyzed from an engineering standpoint by Donnell.[6]

It might be anticipated that the velocity of the retraction wave would be essentially constant if the band is uniform in cross section. Measurements of the velocity at different states of retraction (made by positioning the light and photocell assembly at different points along the strip)

show that the velocity actually increases slightly as the retraction progresses. This is illustrated in Fig. 5. A probable explanation for this is that the small "dead" mass held in grip No. 1 retards the retraction at first.

The retraction wave can be shown very plainly by means of photographs taken with a high speed stroboscopic light of the Edgerton type. Some typical photographs are shown in Figs. 6a and 6b. The first picture is a balloon in the act of bursting. A faint outline of the original shape can be seen. The retraction wave has advanced about halfway down the sides of the balloon, so that the lower half of the balloon is as yet unaware that it has been pricked by the pin. A retracting steel spring is shown for comparison with rubber. In Fig. 6b, the very broad wave front of butyl gum stock is seen in contrast to the sharp front for Hevea gum stock in four stages of retraction.

The local elongation along some of the retracting strips, obtained by measuring the distances between the ruled lines on the photographs, has

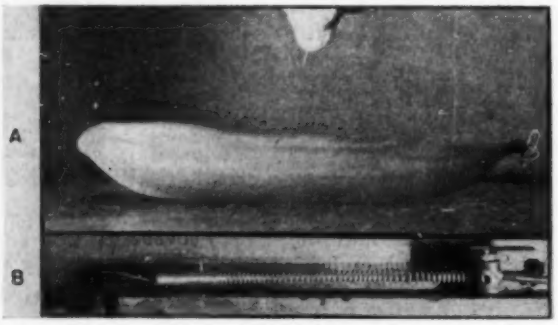

FIG. 6a. High speed photographs of rubber in retraction. *A*, balloon bursting. *B*, steel spring, about 35 percent retracted.

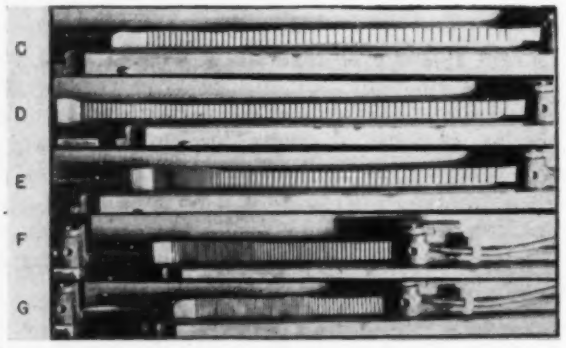

FIG. 6b. *C*, Butyl gum stock, about 30 percent retracted. *D*, Hevea gum stock, about 5 percent retracted. *E*, Hevea gum stock, about 40 percent retracted. *F*, Hevea gum stock, about 55 percent retracted. *G*, Hevea gum stock, about 70 percent retracted.

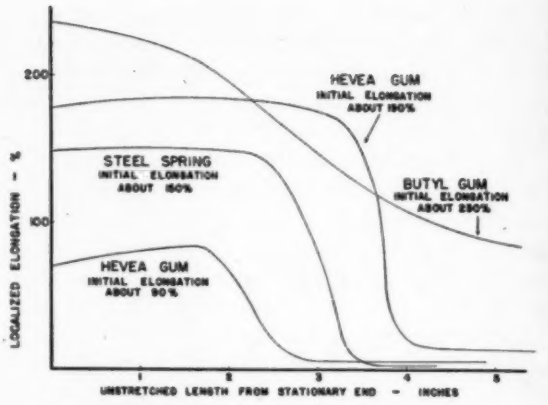

FIG. 7. Local elongation *vs.* unstretched length.

been plotted in Fig. 7. This plot shows more clearly the sharp wave front of the Hevea gum and the steel spring. The Butyl rubber, on the other hand, having a high internal friction and low resilience, has a broad wave front which amounts simply to a gradual reduction in elongation along the entire length of the strip.

The form of the retraction is predicted by the classical theory of a vibrating bar.[7,8] The familiar wave equation which applies is

$$\frac{\partial^2 u}{\partial t^2} = v^2 \frac{\partial^2 u}{\partial x^2}. \tag{1}$$

Here u is the displacement and $v[=(E/\rho)^{\frac{1}{2}}]$ is the retraction wave velocity. E is Young's modulus and ρ is the density.

To simplify the boundary conditions, the case of a stretched rubber strip, the two ends of which are released simultaneously, was considered. Since the center of the strip remains at rest, the description of the retraction of one-half of the strip applies to our experiments.

The boundary conditions are

$$u=0 \text{ at } x=L/2;$$
$$\partial u/\partial x=0 \text{ at } x=0 \text{ or } L;$$
$$\partial u/\partial t=0 \text{ at } t=0;$$
$$u=(-\epsilon L/2)+\epsilon x \text{ at } t=0.$$

The solution was found to be

$$u=\sum_{n=1,3,5\cdots}^{\infty} \frac{4\epsilon L}{n^2\pi^2} \cos\frac{n\pi x}{L} \cos\omega_n t. \tag{2}$$

L is the length of the strip, ϵ or $(\partial u/\partial x)_{t=0}$ is the unit elongation, and $\omega_n = n\pi v/L$.

The following numerical values were used as typical for Hevea gum stock: $E=9.6$ kg/cm², $\rho=0.92$ g/cm³, $L=25.4$ cm, $\epsilon=3$ (300 percent

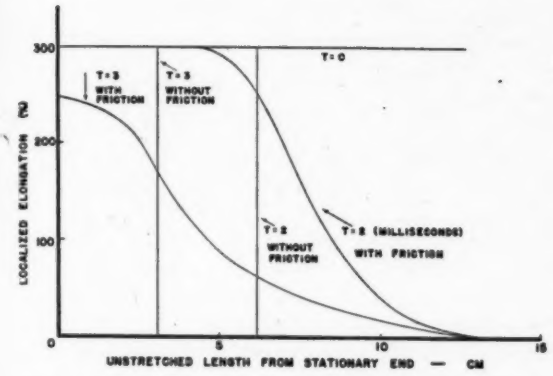

FIG. 8. Theoretical curves with and without friction.

elongation). Good convergence was obtained by using five terms of the series.

To compare the shapes of the calculated wave fronts with those observed experimentally, it was necessary to differentiate u with respect to x for fixed values of t. This gives the local elongation as a function of the distance from one end. The sharp wave fronts calculated for three values of the time are shown in Fig. 8 and are similar to those observed for Hevea gum stock and plotted in Fig. 7.

If a viscous friction term, $2k(\partial u/\partial t)$, is included in the left-hand side of Eq. (1), the solution is, for the same boundary conditions as before,

$$u=\sum_{n=1,3,5\cdots}^{\infty}\frac{4\epsilon L}{n^2\pi^2}e^{-kt}\cos\frac{n\pi x}{L}\frac{\cos(\omega_n t-\phi_n)}{\cos\phi_n}. \quad (3)$$

Here

$$\phi_n=\tan^{-1}\left(\frac{k}{\omega_n}\right), \quad \text{and} \quad \omega_n=\left[\left(\frac{n\pi v}{L}\right)^2-k^2\right]^{\frac{1}{2}}.$$

Using the same numerical values as before and $k=300$ sec.$^{-1}$, the plots for $\partial u/\partial x$ for t equal to 2 and 3 milliseconds are given in Fig. 8. They show a broadening of the wave front as compared to the case calculated without friction. From comparison of the calculated and observed wave fronts, it appears that the value selected for the friction was considerably less than the actual friction for Butyl gum stock and somewhat larger than that for Hevea gum stock.

The velocity actually measured is not that of the wave front, for which $v=(E/\rho)^{\frac{1}{2}}$ but is that of the end of the strip. The relationship between the two may be obtained to a first approximation by assuming that the potential energy of the stretched strip is all converted into kinetic energy. For a strip of unit cross-sectional area,

$$\text{P.E.}=E\epsilon\frac{1}{l}\int_0^l \epsilon x dx,$$

where E is the elongation and l the unstretched length.

$$\text{K.E.}=\tfrac{1}{2}mv_m^2=\frac{l\rho}{2}v_m^2,$$

where v_m is the measured velocity.

Equating these quantities gives:

$$v_m=\epsilon(E/\rho)^{\frac{1}{2}}=\epsilon v.$$

Assuming a constant modulus (Hooke's law) and density per unit length (based on unstretched dimension) the velocity v_m should be directly proportional to the elongation and to the square root of the modulus divided by the density. These are reasonable assumptions because the modulus of a good gum stock, such as Hevea, is nearly constant up to several hundred percent elongation. However, there are several other factors which are not considered by this simple relationship. The internal friction will reduce the velocity somewhat. The mass of that part of the strip held

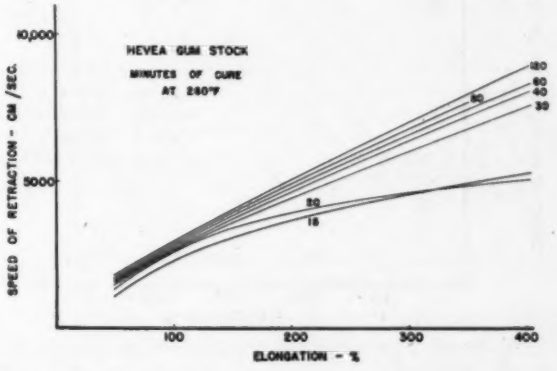

FIG. 9. Speed of retraction *vs.* elongation.

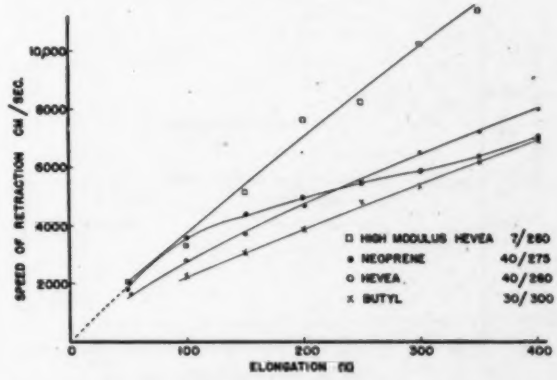

FIG. 10. Speed of retraction of gum stocks *vs.* elongation.

TABLE I. Parts by weight.

Compound	*A*	*B*	*C*	*D*	*E*	*F*	*G*	*H*
Smoked sheet	100.0	100.0	100.0	100.0				
GR-S					100.0	100.0	100.0	100.0
Captax	1.35	1.35	1.35	1.35	1.5	1.5	1.5	1.5
Stearic acid	3.0	3.0	3.0	3.0	2.0	2.0	2.0	2.0
Zinc oxide	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
Softener	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0
Sulfur	2.75	2.75	2.75	2.75	2.0	2.0	2.0	2.0
Easy processing Channel black	50.27	40.22	30.16	20.11	59.00	49.20	39.40	19.70

by grip No. 1 will provide additional inertia which will reduce the velocity measured. Plastic flow and the sidewise motion of the elements of the strip in expanding to the unstretched width would have a similar effect. The velocity would also be reduced by the reduction of modulus caused by the Joule cooling of the strip owing to the adiabatic contraction. For Hevea gum stock, the measured velocities are actually somewhat higher than those calculated from stress-strain data.

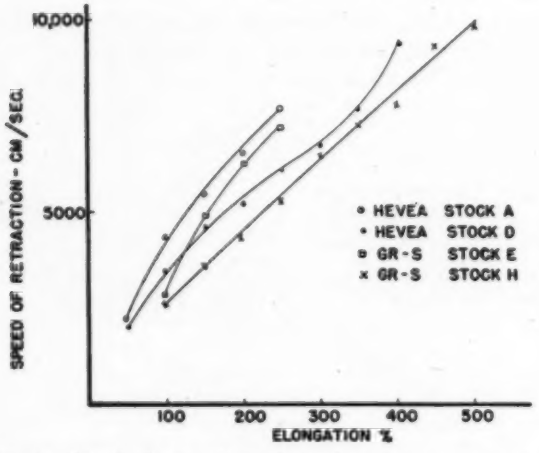

FIG. 11. Speed of retraction of tread stocks *vs.* elongation.

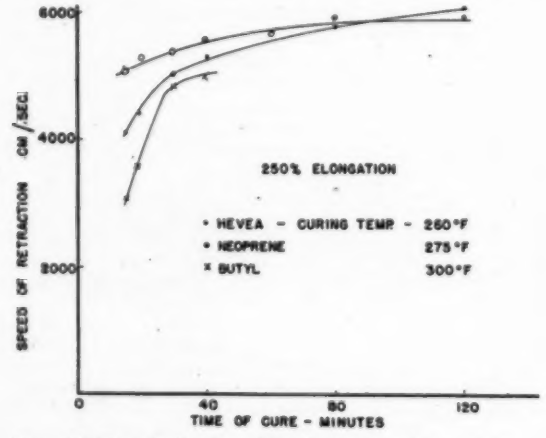

FIG. 12. Speed of retraction of gum stocks *vs.* cure.

This is probably associated with the fact that the modulus of rubber increases with the testing speed.

COMPOSITION OF STOCKS

In order to compare the effect of carbon black loading in stocks, a series of natural rubber and GR-S stocks was compounded as shown in Table I.

The compositions of the gum stocks tested are given in Table II.

In order to note the effect of mixing GR-S and Hevea, a series of stocks was compounded using a good GR-S tread stock as a base, with different percentages of Hevea added. The acceleration of the stocks was adjusted to give the same rate of cure. Thus the 100 percent Hevea stock is not a typical tread stock, and this fact should be considered when comparing its properties with the other stocks. The compositions are given in Table III.

The stocks of Tables I and II were formulated by J. H. Fielding and those of Table III by E. Cousins.

DISCUSSION OF MEASUREMENTS

The velocity of the retraction of a rubber strip is obviously dependent upon the density and modulus of the stock. Other important factors are the internal friction, plastic flow, and stress relaxation of the material before it is released. These effects are illustrated by plots of data obtained under various conditions.

Figure 9 shows the rise in speed of retraction with elongation. These curves are almost straight lines, quite different from the ordinary stress-strain curves, showing that other factors beside the modulus affect the speed of retraction. There is a definite change in slope of all the curves between 0 and 100 percent elongation which may be related to the shape of the stress-strain curve. The continued curvature of the two undercured samples is undoubtedly due to the high plastic flow of these stocks.

TABLE II. Parts by weight.

Compound	*N*	*O*	*P*	*Q*
Smoked sheet (Hevea)	100.0	100.0		
GR-I (Butyl)			101.5	
GR-M (Neoprene)				100.0
Captax[1]	.5		.5	
Tuads[2]			1.0	
P.P.D.[3]		2.0		
Stearic acid	1.0			.5
Zinc oxide	5.0	2.0	5.0	5.0
MgO				4.0
Phenyl α-naphthylamine				2.0
Sulfur	3.0	2.0	2.0	

[1] Captax: 2-Mercaptobenzothiazol.
[2] Tuads: Tetramethylthiuram disulfide.
[3] P.P.D.: Piperdinium pentamethylene dithio carbamate.

TABLE III. Parts by weight.

Compound	*I*	*J*	*K*	*L*	*M*
GR-S	100	75	50	25	
Smoked sheet		25	50	75	100
Santocure[1]	1.6	1.3	1.0	.75	.5
Stearic acid	1.0	1.0	1.0	1.0	1.0
Zinc oxide	3.0	3.0	3.0	3.0	3.0
Softener	4.0	4.0	4.0	4.0	4.0
Sulfur	1.6	2.0	2.3	2.65	3.0
Easy processing Channel black	45	45	45	45	45

[1] Benzothiazyl 2-monocyclohexyl sulfenamide.

Figure 10 shows how Hevea rubber compares with synthetic polymers. The Neoprene stock gives a comparatively high velocity at low elongations, but the higher internal friction of this stock and of the butyl stock results in lower velocities at high elongation.

Figure 11 shows the effect of elongation on the speed of retraction of loaded stocks. These curves are very nearly straight lines. The high forces required to give the elongations above 300 percent may have resulted in slippage at the grips so that there is some scattering of the points. Until a better means of clamping the test strips has been devised, no attempt to interpret such small deviations will be made.

One of the most dependable criteria for state of cure, even though not "scientific," is the "snappy" feel of the stock. Few quantitative tests are available which give a definite means of determining the best cure for general purposes if the stock is not compounded for a specific property such as tensile strength. One of the important results of curing a stock is the reduction of plastic flow and the increase in modulus. Since the speed of retraction is so greatly affected by these properties, it seems likely that it should show the difference between a properly cured and undercured stock.

Figures 12 and 13 are plots of speeds of retraction for various cures for typical stocks. Although the Neoprene gum stock does not show a large effect, there is a more or less sharp bend in each of the curves for the other stocks. The bend is a result of the reduction in plasticity of the stocks as the cure proceeds, which is accompanied by increasing modulus and decreasing internal friction. In every case it appears at approximately the curing time denoted by the compounders as the "best" cure. The position of this bend in the plots is not greatly affected if the 30 seconds allowed for the strip to come to equilibrium before releasing from the grips is increased to two minutes. However, the angle of the bend is in creased so that the point of "best" cure is less definite.

In order to determine the effect of temperature on the speed of retraction, the apparatus was placed in an enclosure so that the temperature of the air surrounding the test piece could be controlled. The strips were conditioned at the desired temperature before stretching. Figure 14 shows the effect of temperature on the speed of retrac-

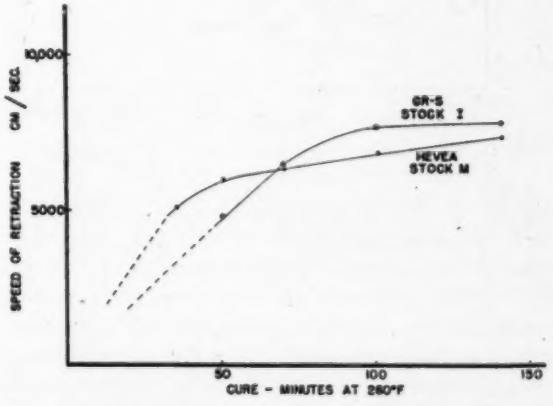

FIG. 13. Speed of retraction of tread stocks *vs.* cure, 250 percent elongation.

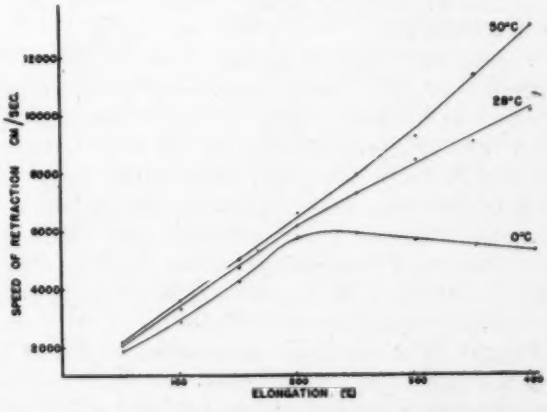

FIG. 14. Speed of retraction *vs.* elongation at different temperatures.

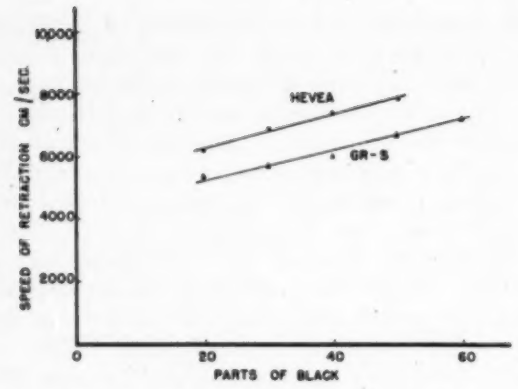

FIG. 15. Speed of retraction *vs.* loading.

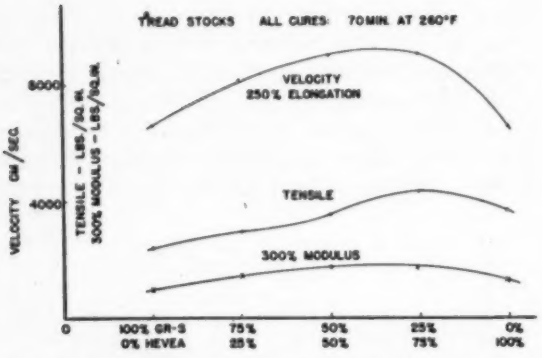

FIG. 16. Effect of adding Hevea in a GR-S compound.

tion for a Hevea gum stock. The reduction in speed at low temperatures for this stock might be explained as caused by an increased permanent set and internal friction of the stock and an increased crystallization. At higher temperatures, increased retractive force increases the speed of retraction. The reduction in velocity of the Hevea gum stock beyond 200 percent elongation at 0°C is evidently due to the formation of crystallites. Several checks were made to make certain of this unexpected behavior.

Figure 15 illustrates the effect of loading with carbon black. The speed of retraction rises almost linearly with loading, although much less rapidly than the modulus does, due to the fact that the internal friction also increases. Differences in internal friction rather than modulus are responsible for the lower velocities of GR-S as compared to Hevea in this plot. The data for Fig. 15 were secured for the stocks of Table I at 250 percent elongation and best cure.

Figure 16 shows how various properties of a GR-S tread stock are affected by substituting increasing percentages of natural rubber for the synthetic polymer. As stated before, the 100 percent Hevea rubber stock is not typical of a natural rubber tread stock but is the result of the consistent compounding used in the series. The apparently inferior properties are not to be encountered in normal practice. The main purpose of this chart is to show how the speed of retraction varies with other standard properties. It may be observed in general that the speed of retraction test appears to be more sensitive than the other tests under selected conditions. Its ultimate value will probably depend upon the results of more critical experiments in the fields where this survey indicates that it may have some usefulness. Under proper circumstances, there is a possibility that it could become a useful criterion for quality and cure.

CONCLUSIONS

The results obtained with this apparatus show that interesting information can be obtained by making measurements of the speed of retraction under various conditions and by comparing different compounds and polymers. This information should be of value both for a better understanding of the molecular structure and the forces involved and also as a practical means for properly qualifying the material as to its elastic properties.

The device appears to have an immediate practical application as an aid to the compounder in determining the "best" cure.

The apparatus is quite simple to use and if properly designed is sturdy and dependable. Reliable measurements could be made at the rate of about fifty per hour without requiring much skill. Thus, the speed of retraction measurement would be practical for a routine, standard test.

ACKNOWLEDGMENT

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Some Relations Between Stress, Strain, and Temperature in a Pure-Gum Vulcanizate of GR-S Synthetic Rubber*

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Stress-temperature relations at constant elongation and at constant length have been studied in a pure-gum vulcanizate of GR-S. Such studies yield information useful for calculations involved in the theory of its elastic behavior, and furnish practical data regarding its tensile properties at different temperatures. The compounding recipe was: 100 parts by weight of GR-S, 2 parts of sulfur, 1 part of zinc oxide, and 0.5 part of zinc dibutyl dithiocarbamate. The specimens were first held at constant length and constant temperature for a period of ½ hour to 2 hours, after which time the effects of relaxation of stress during the observation of stress-temperature relations were negligible. The value of the stress after relaxation at each elongation was used to plot a stress-strain curve. The stress-temperature relations observed for temperatures below the relaxation temperature were linear and reproducible on successive runs of increasing and decreasing temperature. When the temperature was raised above the relaxation temperature straight lines were not obtained, since further relaxation occurred at the higher temperatures. The intercepts at 0°K for the lines obtained below the temperature of relaxation are useful in evaluating the internal energy changes. The intercepts of the lines representing the experiments at constant elongation were found to be negative. The absolute values were of the order of 10 percent of the stress after relaxation for the lowest elongations, and increased to almost 30 percent of the stress at the highest elongation.

I. INTRODUCTION

SOME relations between stress, strain, and temperature have been investigated for a pure-gum vulcanizate of GR-S synthetic rubber in order to furnish experimental information for use in theoretical consideration of its elastic behavior. The results of the work also yield some practical information about the tensile properties at high and low temperatures.

In this work stress was studied as a function of temperature, keeping the elongation, or sometimes the length, constant. In this way effects of friction and flow accompanying changes in length of specimens were minimized.

The general methods employed in this study were first outlined by Meyer and Ferri,[1] who in common with other observers[2–4] applied them to natural rubber. Peterson, Anthony, and Guth[5] in the only studies of this sort dealing with synthetic rubber did not include GR-S or other butadiene-styrene copolymers.

* Presented on June 24, 1944 before the Inaugural Meeting of the Division of High-Polymer Physics of the American Physical Society at Rochester, New York.

II. EXPERIMENTAL PROCEDURE

1. Compound and Cure

The compound was prepared according to the following recipe:

	Parts by weight
GR-S	100
Sulfur	2
Zinc oxide	1
Zinc dibutyl dithiocarbamate (butyl zimate)	0.5
Total weight of compound	103.5.

This recipe was selected because it seemed to involve the addition of about a minimum quantity of compounding ingredients to the raw GR-S to produce a well-vulcanized product. The GR-S employed for part of this investigation was received in January, 1943 from the Rubber Reserve Company plant operated by the Goodyear Company in Akron, Ohio. GR-S employed for the remainder of this investigation was prepared for the Office of the Rubber Director and labeled ORD No. 45. The compounds were vulcanized in the form of sheets, of which some were about 0.065 inch thick and others were about 0.080 inch thick. The curing conditions were chosen to give a vulcanizate of approximately maximum stiff-

ness. At 292°F this required 35 minutes and 25 minutes, respectively, for the Goodyear GR-S and ORD No. 45.

2. Specimens

The GR-S specimens were in the form of flat strips or dumbbells ½ inch wide and measuring 2 inches, 10 centimeters, or sometimes 20 centimeters between gauge marks. They were stretched by dead-weight loading with manual control of the elongation, which could be observed by

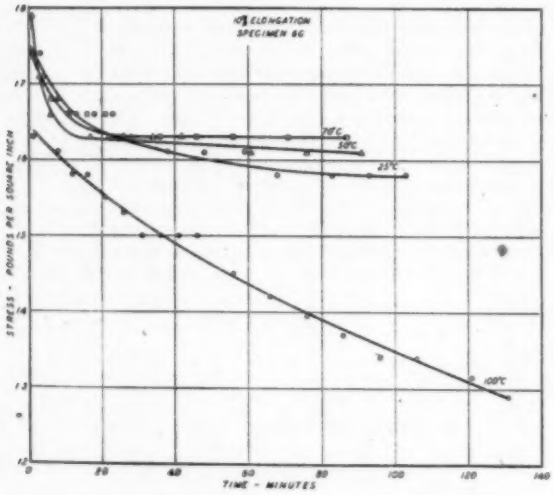

FIG. 1. Stress-time relations for an elongation of 10 percent. The tests were conducted in the order of increasing temperature.

means of displaceable fiducial marks and a graduated scale viewed through a glass window.

The specimens, fiducial marks, and scale were contained in an enclosure through which a vigorous current of air was circulated by a blower. The air was heated by resistance coils of the type used in radiant heaters or cooled by the use of dry ice. Consequently at the lower temperatures the specimens were surrounded by an atmosphere containing large amounts of carbon dioxide. No effects ascribable to the carbon dioxide were noted.

3. Definitions of Constant Elongation and Stress

Stress-temperature studies on the Goodyear GR-S were all made with the specimens held at constant elongation. Studies on the ORD No. 45 were made both for constant length and for constant elongation.

For the portion of the work where the elongation was kept constant, the percentage elongation was always measured with reference to the unstretched length at that particular temperature. In other words, as the temperature was varied the distance between gauge marks was not held constant, but was kept proportional to the unstretched length at each temperature. Consequently the elongation, as just defined, was maintained constant as the temperature was varied. In order to obtain this constant elongation the distance between the gauge marks on an unstretched specimen was measured over the whole range of temperatures studied so that all elongations could be referred to the corresponding unstretched lengths at each temperature. There was moderately good agreement between the measured unstretched lengths and those calculated by the use of the linear expansivity, 220×10^{-6} per °C, commonly employed in this laboratory for pure-gum vulcanizates of natural rubber.

The stress is defined for the purposes of the present work, in accordance with the usual practice, as the force per unit area of original cross section (the area being measured at room temperature).

4. Relaxation of Stress

In order to minimize the effects of relaxation of stress during the observations of stress-temperature relations, the specimens were first stretched to the desired elongation and held at a constant temperature for a period of ½ hour to 2 hours. It was found that after this treatment no further relaxation occurred during the stress-temperature studies.

5. Stress-Temperature Relations

The stress-temperature relations were investigated only for temperatures below the temperature at which the relaxation occurred. The temperature was lowered by steps to the neighborhood of −20°C and the loads were reduced so as to maintain constant elongation or constant length. Finally the temperature was again raised and the load increased. When the increase of temperature yielded the same values of stress which had been obtained with decreasing temperatures, it was concluded that no appreciable relaxation or flow had occurred during the cycle of temperature variation.

6. Set

At the conclusion of a stress-temperature cycle the load was removed and the distance between the gauge marks was measured, using a magnifying glass and a steel scale graduated in hundredths of an inch. When the increase in the distance over that measured at the beginning of the experiment was greater than 0.2 percent, the specimen was discarded after a determination of its permanent set. The term permanent set is used in this paper as a measure of the percent increase in length of the unstretched specimen which remains after it had been heated in the unstretched state to about 100°C for a few minutes and then stored for one or two days at room temperature. When the initial set was less than 0.2 percent it was considered negligible and the specimen was sometimes used for further experiments.

III. RESULTS

1. Relaxation of Stress

The relaxation of stress with time, observed at constant temperatures, is shown for elongations of 10 percent and 50 percent in Figs. 1 and 2, respectively. It will be noted that for temperatures of 25°, 50°, and 70°C the rate of decrease of stress becomes relatively small after about 20 minutes and approaches a more or less constant or equilibrium value. At 100°C, however, the rate did not decrease appreciably, even after two hours. Relaxations at this temperature were also accompanied by large permanent set which is an indication of flow. The exactness of approach of the stresses to an equilibrium at temperatures of 70°C and below was not investigated for times longer than about two hours, since the only aim was to have no appreciable further change with time during observations of stress-temperature relations.

The values of stresses observed after relaxation at various elongations and temperatures are listed in Table I and are used to plot the stress-strain curve shown in the upper part of Fig. 6. In this figure the stresses after relaxation at 20°C and 30°C may, for all practical purposes, be considered the same as if the relaxations had occurred at 25°C. The stresses after relaxation at 70°C are only slightly higher than those for 25°C. Inasmuch as the stresses at 50°C lie between those at 25°C and those at 70°C, they are not shown on the graph. However, at 70°C the specimens broke during the relaxation period when the elongation was greater than 50 percent.

TABLE I. Results of stress-temperature studies after relaxation at constant elongation.

Specimen number	Elongation	Temperature of relaxation	Stress at temperature of relaxation	Values from stress-temperature curves for constant elongation: Slope	Values from stress-temperature curves for constant elongation: Intercept at 0°K
	%	°C	lb. in.$^{-2}$	lb. in.$^{-2}$ deg.$^{-1}$	lb. in.$^{-2}$
6*G*	10	25	15.8	0.071	−6.4
7*G*	20	25	27.1	0.104	−3.9
2*G*	35	25	39.9	0.164	−9.0
9*G*	50	25	51.0	0.191	−5.9
10*G*	75	25	65.8	0.268	−14.1
6*F*	100	30	74.8	0.296	−14.9
3*E*	125	25	85.0	0.366	−24.1
8*D*	150	20	90.5	0.414	−30.8
10*F*	150	20	95.7	0.412	−25.0
6*G*	10	50	16.1	0.065	−4.9
7*G*	20	50	28.0	0.096	−3.0
8*G*	35	50	41.4	0.149	−6.7
9*G*	50	50	51.7	0.180	−6.4
8*F*	75	40	65.2	0.255	−14.6
6*G*	10	70	16.3	0.057	−3.3
4*F*	20	70	28.3	0.093	−3.6
8*G*	35	70	42.8	0.140	−5.2
9*G*	50	70	53.7	0.174	−6.0

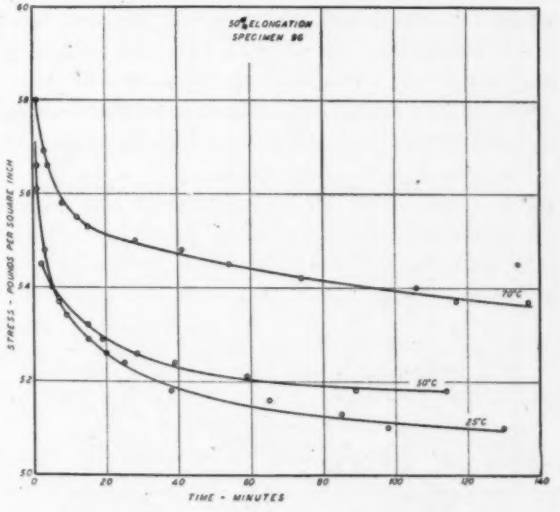

FIG. 2. Stress-time relations for an elongation of 50 percent. The tests were conducted in the order of increasing temperature.

2. Stress-Temperature Relations

Typical results of stress-temperature relations in which the elongation was held constant are shown in Figs. 3 and 4. The data represented by the uppermost curves in Figs. 3 and 4 were obtained after carrying out the relaxation at 25°C

shown in Figs. 1 and 2, respectively. The vertical lines at the upper end of each curve represent the decrease in stress during the relaxation. Stresses obtained as the temperature was lowered are represented by circles on the graph. Stresses observed as the temperature was increased are shown by crosses. The second and third curves in Figs. 3 and 4 were obtained in a similar manner after relaxations at 50°C and 70°C, respectively. The fourth curve in Fig. 3 was obtained after the relaxation at 100°C shown in Fig. 1. The value of permanent set at the conclusion of this experiment was about 2 percent, whereas the values after similar experiments at 70°C were of the order of 0.5 percent. No further experiments were conducted at 100°C.

A linear relation between stress and temperature was invariably obtained. Repeated cycles of variation of temperature produced the same values of stress. Within the limits of observation the stress was now found to be no longer a function of time but to depend solely upon the elongation, the temperature, and the temperature at which the relaxation had occurred. If the temperature was raised above that at which relaxation had occurred, straight lines were not obtained, since further relaxation occurred at these higher temperatures, and the stress became again dependent upon the time. After relaxation the straight lines could be obtained as before by lowering the temperature. It can be noted from Figs. 3 and 4 that the value of the stress at a given temperature and the slope of the stress-temperature lines depend upon the temperature at which the relaxation occurred.

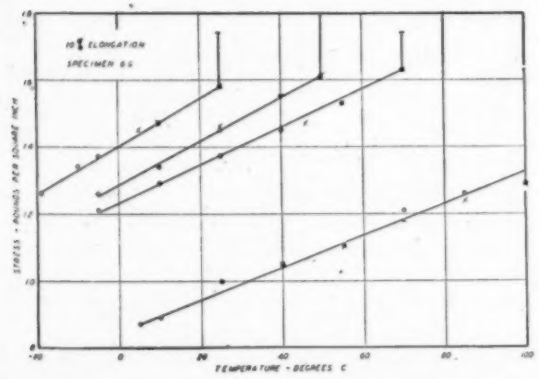

FIG. 3. Stress-temperature relations for an elongation of 10 percent. Each stress-temperature relation was obtained after the corresponding relaxation shown in Fig. 1. The vertical line at the point of the highest temperature shows the amount of relaxation and the temperature at which it occurred.

The same stress-temperature lines were obtained after relaxation at 70°C regardless of whether or not relaxation at 25°C had occurred previously. However, after relaxation at 70°C a recovery period during which the rubber remained unstretched was required before the values corresponding to the original relaxation at 25°C could be again obtained. This recovery period was of the order of days at room temperature, but could be very considerably reduced if the unstretched rubber were heated above room temperature. In the following work, however, when data for different relaxation temperatures are reported for the same specimen, the data for the lower relaxation temperatures were always observed first.

Figure 5 shows stress-temperature relations for various elongations. Except for two of the curves shown, the relaxations were conducted at 25°C. Difficulty in finding a specimen which would not fail at 150 percent elongation during the relaxation at 25°C led to the use of a relaxation temperature of 20°C for this elongation. The relaxation at 100 percent elongation was carried out at 30°C.

It will be noted that the slopes of the lines representing the stress-temperature relations are greater at the higher elongations. When the lines were extrapolated to 0°K, they were observed to have negative intercepts on the stress axis. These intercepts are shown graphically in the lower portion of Fig. 6. The extrapolation is carried out for the purpose of furnishing data for theoretical calculations and, of course, in no way assumes that the actual stress-temperature relation is linear for GR-S at temperatures below those which were investigated.

From our definition of constant elongation it follows that the curve representing the stress-temperature intercepts should pass through zero at zero elongation. This conclusion is evident when we note that for a constant elongation equal to zero the stress should always be zero. The corresponding stress-temperature graph then coincides with the temperature axis, and its intercept, of course, is zero. The intercept curve in Fig. 6 is drawn through the origin and is a straight line. This line seems to represent the data within the experimental errors.

Table I presents for various elongations and for various relaxation temperatures the values of stresses after relaxation, the slopes of the stress-temperature lines, and their intercepts. It can be seen from this table that the stresses after relaxation increase somewhat with increasing tempera-

ture, and the slopes of the stress-temperature lines decrease with increasing temperature of relaxation. The uncertainty in the results does not warrant any definite conclusions on the effect of temperature on the intercepts.

3. Permanent Set

The permanent set for experiments reported in Table I ranged from negligible values to as high as 1.5 percent. In experiments where the relaxation temperature was 20°C to 30°C the permanent set was less than 0.5 percent for elongations up to 75 percent. The set was about 1 percent for 100 percent elongation and became somewhat greater for higher elongations. Where the relaxation temperature was 40°C or 50°C the set ranged from less than 0.5 percent to 1 percent. Where the relaxation temperature was 70°C the set became as great as 1.5 percent at an elongation of 50 percent.

4. Equilibrium Stress-Strain Curves

It has been pointed out that during the relaxation of stress at constant elongation and constant temperature the stress decreases, approaching fairly near to constancy after a period ranging from ½ hour to 2 hours. In these experiments the specimens had not been stretched previously to an elongation greater than that under study. In a few additional experiments, however, the change of stress with time was investigated after the specimen had been maintained for some time at a greater elongation. The stress was found to be considerably lower at first than the lowest value attained in the previous experiments, but it now increased with time and approached the same final value. No detailed investigation of this effect was made to determine the effects of extended periods of relaxation. However, since the value of the stress after relaxation may be approached from either direction, it will be regarded for the purposes of this paper as an equilibrium value. The curve obtained when such values are plotted against the corresponding elongations is then an "equilibrium" stress-strain curve. The upper curve of Fig. 6, plotted from data in Table I, is a typical graph of this sort.

Our studies of various samples of GR-S have shown differences in the stress-strain properties of different specimens, even when they are cut from the same sheet of vulcanizate. This non-uniformity is found to be present also for stresses observed after relaxation, and accounts for some of the variations shown in Fig. 6 and Table I, where each value was obtained from a different specimen. In order to minimize these variations and to obtain an equilibrium stress-strain curve for a single specimen, studies were made for a series of elongations of one specimen. In this study the specimen was first allowed to relax at the lowest elongation to be studied. Then after recording the equilibrium stress the load was increased and the specimen allowed to relax at the next elongation. The data for such a stress-strain curve obtained from a specimen of the ORD No. 45 GR-S is shown in Table II and plotted in

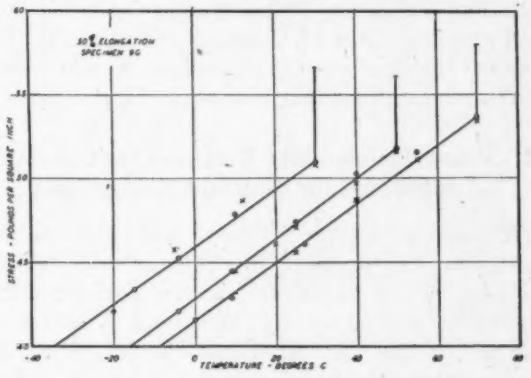

FIG. 4. Stress-temperature relations for an elongation of 50 percent. Each stress-temperature relation was obtained after the corresponding relaxation shown in Fig. 2. The vertical line at the point of the highest temperature shows the amount of relaxation and the temperature at which it occurred.

TABLE II. Results of stress-temperature studies on a single specimen. The relaxations were conducted at 30°C.

Elongation	Stress at 30°C	Values from stress-temperature curves: Constant length Slope	Constant length Intercept at 0°K	Constant elongation Slope	Constant elongation Intercept at 0°K
%	lb. in.$^{-2}$	lb. in.$^{-2}$ deg.$^{-1}$	lb. in.$^{-2}$	lb. in.$^{-2}$ deg.$^{-1}$	lb. in.$^{-2}$
5	8.5				
7.5	12.3				
10	16.0	0.0276	+7.7	0.0685	− 4.7
12.5	18.6				
12.5[a]	18.6				
15	22.0				
17.5	24.6				
20	27.4	0.0672	+7.0	0.101	− 2.3
25	32.4				
30	37.2				
35	42.1				
35[a]	41.1	0.130	+1.9	0.158	− 6.7
40	45.1				
45	48.6				
50	52.5	0.172	+0.4	0.20	− 8.1
50[b]	54.9				
60	60.3				
75	69.4	0.236	−2.3	0.266	−11.4
100	83.2	0.302	−8.1	0.338	−19.1
125	93.5				

[a] Specimen was allowed to relax over night.
[b] Load was removed for 40 hours previous to a relaxation period of 1½ hours.

the upper part of Fig. 7. The points shown in this figure as triangles and squares refer to other specimens. In Table II it will be noted that at elongations of 12.5 percent and 33 percent no great change in stress was observed even when the specimen was allowed to relax over night. At 50 percent elongation the load was removed for 40 hours and a new value of stress was observed and recorded after 1½ hours of relaxation. At 125 percent elongation the specimen broke before stress-temperature relations could be observed.

5. Stress-Temperature Relations for Constant Length and for Constant Elongation

Stress-temperature relations were also studied as before except that the process was carried through two cycles of temperature variation. For one cycle the elongation was kept constant as before, and for the other one the length of the specimen was kept constant. The results of an experiment of this kind are also shown in Table II, and the intercepts are plotted in the lower part of Fig. 7.

Figure 8 and Table III show similar data ob-

TABLE III. Results of stress-temperature studies on a single specimen. The relaxations were conducted at 0°C.

Elongation	Stress at 0°C	Values from stress-temperature curves: Constant length Slope	Constant length Intercept at 0°K	Constant elongation Slope	Constant elongation Intercept at 0°K
%	lb. in.$^{-2}$	lb. in.$^{-2}$ deg.$^{-1}$	lb. in.$^{-2}$	lb. in.$^{-2}$ deg.$^{-1}$	lb. in.$^{-2}$
5	8.5				
10	15.2				
20	26.9	0.066	+8.9	0.108	− 2.6
30	36.2				
35	39.9	.127	+5.2	.158	− 3.2
50	50.6	.168	+4.4		
50[a]	50.9				
100	76.9	.276	+1.5	.328	−12.7
150	98.4	.380	−5.2		
200	125				

[a] Load was removed for 17 hours previous to a relaxation period of 50 minutes.

served for a relaxation temperature of 0°C. At 50 percent elongation the load was removed after relaxation and observation of the stress-temperature relation, and the specimen was allowed to rest over night at room temperature. The temperature was again lowered to 0°C the next morning and the specimen was again allowed to relax at 50 percent elongation. The value shown in Table III was observed after 50 minutes. At 200 percent elongation the specimen broke during the relaxation. The values for the points shown as triangles at 150 percent and 175 percent elongation were observed for another specimen.

At the time that most of the work described in the present paper was performed, it appeared that theoretical interest was largely concerned with stress-temperature relations at constant elongation. Indeed, previous workers,[1,3,5] who had maintained specimens at constant length, introduced corrections to obtain results at constant elongation. However, more recent theoretical interest, as discussed by James and Guth,[6] seems more concerned with stress-temperature relations at constant length. Relatively simple equations can be derived relating the values of slope and intercept obtained by the two methods. The direct experimental comparison of the results obtained on the same specimen by the two methods was made in order to clarify this point.

The values of the intercepts of stress-temperature curves at constant elongation are negative and are nearly proportional to the elongation. The numerical values of the intercepts are of the order of 10 percent of the equilibrium stresses at the lowest elongations, and increase to almost 30 percent at the highest elongations. The values of the intercepts of the stress-temperature curves obtained at constant length are positive at the low elongations and negative at the high.

6. Non-Equilibrium Stress-Strain Relations

Studies were made of the stress-strain relations obtained at −20°, 25°, and 70°C by elongating the specimen at an average rate of about 200 percent per minute and then immediately allowing retraction at the same rate. This rate is between one-quarter and one-half that employed in the usual testing machines. Dead-weight loading was employed in these studies, the stress being varied by increments of about 12.5 lb./in.^{2}.

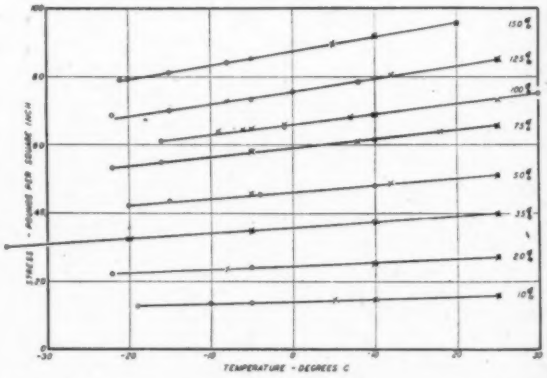

FIG. 5. Stress-temperature relations for various elongations. With two exceptions the relaxation temperature was 25°C. At 100 percent elongation it was 30°C and at 150 percent it was 20°C.

Typical results for a specimen of the Goodyear GR-S are presented in Fig. 9. Two cycles of extension and retraction are shown. The equilibrium stress-strain curve from Fig. 6 is shown as a broken line curve for purposes of comparison. The second extension curve in this study is substantially lower than the first extension curve. The retraction curves for the two cycles differ only slightly. As would be expected, the equilibrium curve lies below the first extension curve, at all elongations. However, higher elongations and stresses are attainable at this speed of stretch than can be maintained during relaxation. Table IV gives for various temperatures the approximate values of the maximum stress and the maximum elongation which are attainable by the two methods of stretching.

TABLE IV. Maximum values of stress and elongation at various temperatures for a stretching rate of about 200 percent per minute compared with the corresponding values after relaxation.

Temperature	Stretched at 200% per minute		After relaxation	
	Maximum elongation	Maximum stress	Maximum elongation	Maximum stress
°C	%	lb. in.$^{-2}$	%	lb. in.$^{-2}$
−20	560	450	—	—
0	—	—	200	125
25	300	150	150	100
50	—	—	70	65
70	160	110	50	55

IV. DISCUSSION OF RESULTS

1. General Comparison with Natural Rubber

The results presented here are similar in many respects to those obtained in this laboratory when similar experiments[4] were conducted with natural rubber. A major difference exists, however, in respect to the phenomena associated with crystallization, which seems to be entirely absent in GR-S and to play a very important part in determining the stress and strain at elongations above 150 percent in the natural rubber compound. For this reason the results of the present work with GR-S are much simpler than those observed with natural rubber. A considerable portion of the present work was completed before the work on natural rubber was begun, and was useful as a guide in showing which results were associated with crystallization. Reference should be made to the paper[4] on natural rubber for a description of the effects of crystallization on the properties under investigation. None of them was ever observed in any of the experiments on GR-S.

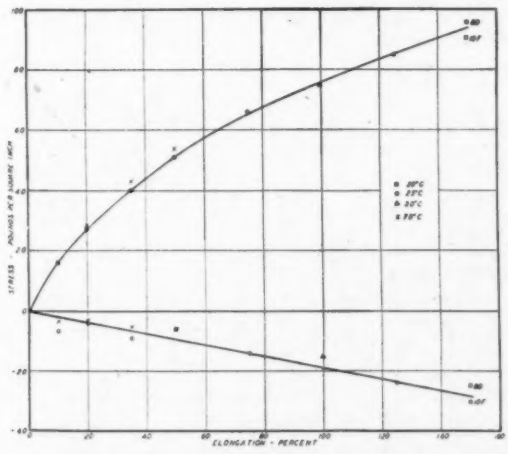

FIG. 6. Stress-elongation relations (upper curve) and stress-temperature intercepts at 0°K (lower curve). The data were observed after periods of relaxation from ½ hour to 2 hours at constant elongation.

2. Temperature of Relaxation

It will be observed from Fig. 1 that at 100°C the stress continues to decrease, the rate of decrease becoming approximately constant. The stress does not approach an equilibrium value, as it does at the lower temperatures.

At a temperature of 70°C and below, it can be seen that this effect is not appreciable, at least during the time of the observations. On the basis of these experiments no further work was done at 100°C since it was desired to avoid effects connected with oxidation. It may be concluded that the temperature at which this becomes appreciable in a few hours is between 70° and 100°C. In natural rubber the corresponding temperature was found to lie between 25°C and 70°C. Much more complete studies of this effect have been made recently by Tobolsky, Prettyman, and Dillon,[7] whose experiments were conducted largely at 100°C and higher temperatures. They have shown that the stress at these temperatures ultimately becomes zero, and have presented convincing evidence that the effect is caused by oxidative scission of the long chain molecules. A theoretical discussion of the causes of relaxation in rubber has been given recently by Mooney, Wolstenholme, and Villars.[8]

3. Stress Relations

The stress may be regarded as a quantity dependent upon the elongation, the temperature, and the previous thermal and mechanical history

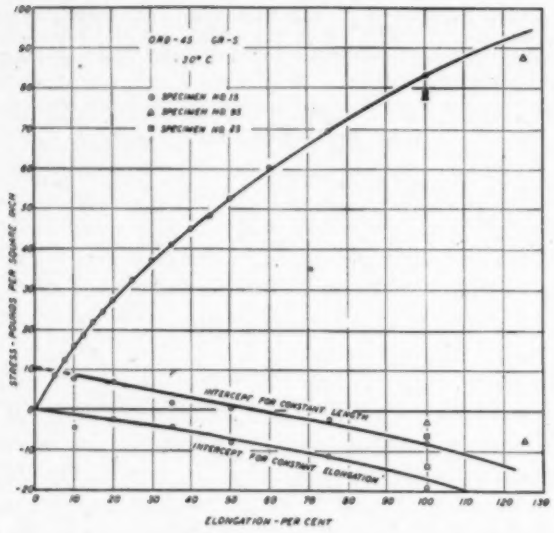

FIG. 7. Stress-elongation relations and stress-temperature intercepts at 0°K. The relaxations were conducted at 30°C. After the desired observations at one elongation the specimen was usually stretched to the next higher elongation without removing the load. Except for the points shown as triangles and squares, the data were all obtained from one specimen.

of the specimen. A brief summary of the results already given will serve to indicate, in a more unified presentation, the nature of this dependence. An effort will be made to present the general features as clearly as possible even at the risk of possible slight inaccuracies arising from second-order effects such as flow or oxidation. The upper limit of temperature in the discussion is taken as 70°C and the lower limit as −20°C.

At temperature T and elongation E there is a corresponding stress value S_E representing an equilibrium condition. The actual value S of the stress at a given time may not equal the equilibrium value S_E because of the previous thermal or mechanical history of the specimen. At room temperatures and above, the stress in the pure-gum GR-S compound studied attains a value within a few percent of S_E in less than two hours after the application of the load. Thereafter there are no further changes with time, provided that the elongation is unaltered and provided that the temperature is not raised above that at which the relaxation occurred. No time effects are introduced by lowering the temperature and then raising it to the relaxation temperature, or by repeating the variation a number of times. The stress-temperature relation under these conditions is linear.

There are evidently two factors having opposite effects on the stress at constant elongation as the temperature is raised above the relaxation temperature. The one is an increase, in accordance with the positive slope of the stress-temperature relation already discussed, and the other is a decrease corresponding to the additional relaxation which occurs at the higher temperature. The two factors nearly counterbalance each other as far as the equilibrium stress at different temperatures is concerned. A slight predominance of the former factor is responsible for the small increase of equilibrium stress with temperature. When the temperature is decreased after relaxation, the stress is affected by only the first factor. As the temperature is increased, the second factor comes into effect only at temperatures above the relaxation temperature. The second factor is time-dependent but becomes approximately constant in a period of the order of hours. The first factor is not time-dependent.

It is evident that measurements of stress-strain isothermals at two different temperatures cannot be used for calculation of the stress-temperature relation at constant elongation, since the changes shown by the isothermals reflect only the difference of the two factors.

A previous heating of the unstretched rubber appears to have no influence, but if the stretched specimen has been heated to a temperature higher than T, or if it has been stretched to a greater elongation than E, and the new condition main-

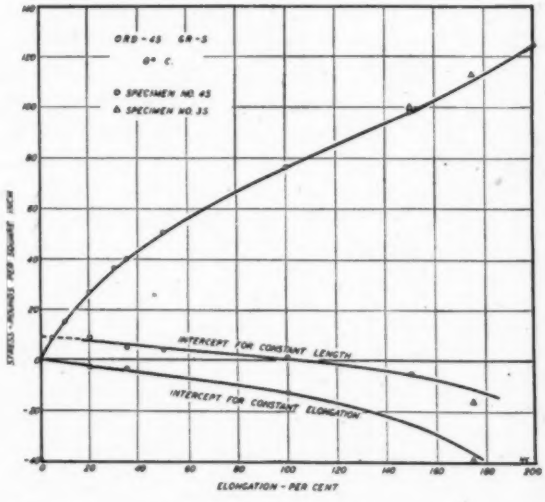

FIG. 8. Stress-elongation relations and stress-temperature intercepts at 0°K. The relaxations were conducted at 0°C. After the desired observations at one elongation the specimen was usually stretched to the next higher elongation without removing the load. Except for the points shown as triangles, the data were all obtained from one specimen.

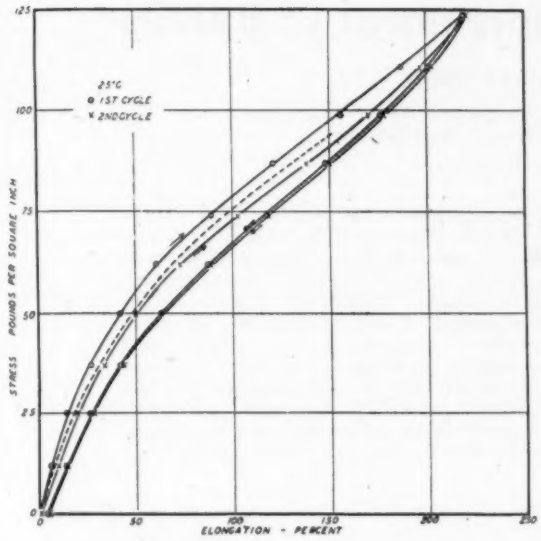

FIG. 9. Stress-elongation relations for extension and retraction at the rate of about 200 percent per minute. There was an interval of about 3 minutes between the two cycles. The broken line shows the stress-elongation curve from Fig. 6 for comparison.

tained for a sufficient time, the stress will be found to be temporarily less than S_E.

It is clear that immediately after any stretching for the first time the stress will be greater than S_E. The first extension curve in Fig. 9 shows higher stresses than S_E at all elongations. The retraction curves in Fig. 9 lie below the S_E curve, but would not have done so if the maximum elongation had been sufficiently small and the rate of elongation sufficiently rapid. The second extension curve, as shown in Fig. 9, is so influenced by the maximum extension and rate of stretch in the first cycle that its position relative to the equilibrium curve cannot be predicted. It is invariably below the first extension curve.

When the load is completely removed from a stretched specimen, S is reduced to zero. This is, of course, less than the S_E corresponding to the residual elongation. Almost all the residual elongation disappears in time under the constant stress of zero because of the influence of the same factors that, at constant elongation, bring about the increase of S to the corresponding S_E after a reduction of elongation.

The values of equilibrium stress are relatively little influenced by temperature. However, the maximum stress and strain are very much affected by temperature, as is evident from Table IV. Consequently, investigations in which relaxation is carried out at low temperatures offer an obvious means of investigating the nature of the equilibrium stress-strain curve at higher elongations than are possible at room temperature.

4. Application of Results

Predictions of the tensile properties of GR-S under different conditions of elongation and at different temperatures may be made by a careful consideration of the phenomena described in the preceding section. Furthermore, results obtained from stress-temperature studies can be utilized, with the aid of thermodynamic equations of the type discussed by Gerke,[9] in evaluating the relative effects of energy and entropy in determining the elastic properties of GR-S. Such a utilization, with the necessary qualifications, is beyond the scope of the present paper, which aims to present only experimental results.

The stress relations just described appear to us to be the fundamental ones associated with the elasticity of any rubberlike material. In natural rubber they are evident at low elongations, but are masked to a certain extent at higher elongations by superposed effects caused by crystallization. A synthetic rubber like GR-S which is free from crystallization offers a particularly favorable medium for studying these effects in their simplest form.

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Limiting Law of the Reinforcement of Rubber*

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The effect of the filler upon the modulus of compounded rubber has been calculated with the aid of some simplifying assumptions. From these calculations it is found that the increase in modulus, caused by the filler, is directly proportional to the volume loading, and is independent of the particle size of the filler. The stress system in the vicinity of a spherical filler particle has also been calculated. A series of experiments has been made to check these calculations. From the results of these experiments, it has been deduced that carbon black is flocculated in rubber; and that P-33, Thermax, and Gilder's whiting are completely dispersed in rubber. These last-named fillers give increases in modulus substantially in agreement with the calculations. It has further been found that Kadox and XX zinc oxide give unusually large increases in modulus. These are ascribed to alteration of the type of cure of the rubber matrix. Catalpo clay showed excessive modulus because of high calender grain.

I. INTRODUCTION

An obvious theoretical approach to the reinforcement of rubber is to analyze the stresses about a filler particle, and from this analysis to deduce the effect of particle size and concentration of filler upon the modulus. Because of the great similarity between the field equations of the theory of elasticity and those of hydrodynamics, this approach is substantially the same as that employed by Einstein[1] in the discussion of increase in viscosity caused by suspension of spherical particles in the liquid.

II. THEORY

Consider a rigid, spherical particle of radius a embedded in rubber of known modulus. We now suppose that the rubber is stretched, and will calculate the displacements and stresses in the vicinity of the solid particle, resulting from this stretch.

The differential equations of equilibrium may be put in the following form:

$$\frac{\lambda+\mu}{\mu}\frac{\partial\Delta}{\partial x}+\nabla^2 u=0,$$

$$\frac{\lambda+\mu}{\mu}\frac{\partial\Delta}{\partial y}+\nabla^2 v=0, \qquad (1)$$

$$\frac{\lambda+\mu}{\mu}\frac{\partial\Delta}{\partial z}+\nabla^2 w=0.$$

In these equations[2] x, y, z are the customary Cartesian coordinates and u, v, w are the vector components of displacement at the point x, y, z. Δ is the cubical dilation and ∇^2 is the Laplacian operator. λ and μ are the elastic constants of the rubber, and are related to Young's modulus M and Poisson's ratio σ by the expressions:

$$M=\frac{\mu(3\lambda+2\mu)}{\lambda+\mu},$$

$$\sigma=\frac{\lambda}{2(\lambda+\mu)}.$$

In order to attack the problem it is necessary to specify the boundary conditions to be fulfilled. The first of these arises from the fact that the influence of the particle will extend only through a limited region of the rubber. At points far distant from the particle, the displacements will correspond to those caused by a simple tension. The second boundary condition is that the displacement at the surface of the solid sphere must vanish, since we assume that there is complete adhesion between the rubber and the filler particle. These boundary conditions may be expressed algebraically by the following equations:

at $r=\infty$

$$u=-\frac{\lambda T}{2\mu(3\lambda+2\mu)}x=-Cx,$$

* Presented on June 23, 1944 before the Inaugural Meeting of the Division of High-Polymer Physics of the American Physical Society at Rochester, New York.

$$v=-\frac{\lambda T}{2\mu(3\lambda+2\mu)}y=-Cy, \qquad (2a)$$

$$w=+\frac{(\lambda+\mu)T}{\mu(3\lambda+2\mu)}z=Az.$$

at $r=a$:

$$u=v=w=0. \qquad (2b)$$

Here T is the tension in the rubber at an infinite distance from the filler particle. The origin of coordinates has been located at the center of the solid sphere, and the Z axis oriented parallel to the direction of stretch. These boundary conditions completely specify the problem. The solution for the displacements is obtained in the form:

$$u=-x\left\{C\left(1-\frac{a^3}{r^3}\right)-B\frac{a^3}{r^3}\left(1-\frac{a^2}{r^2}\right)\left(1-5\frac{z^2}{r^2}\right)\right\},$$

$$v=-y\left\{C\left(1-\frac{a^3}{r^3}\right)-B\frac{a^3}{r^3}\left(1-\frac{a^2}{r^2}\right)\left(1-5\frac{z^2}{r^2}\right)\right\}, \qquad (3)$$

$$w=x\left\{A\left(1-\frac{a^3}{r^3}\right)+B\frac{a^3}{r^3}\left(1-\frac{a^2}{r^2}\right)\left(3-5\frac{z^2}{r^2}\right)\right\},$$

where

$$r^2=x^2+y^2+z^2$$

and

$$B=\frac{3}{4}\frac{T}{\mu}\frac{\lambda+\mu}{3\lambda+8\mu}.$$

In order to apply these results to rubber, it is convenient to introduce the assumption that Poisson's ratio equals $\frac{1}{2}$, as is known to be the case for rubber at small elongations. This assumption is incorporated in our equations by setting λ infinitely large compared to μ. Then

$$A=\frac{1}{3}\frac{T}{\mu},$$

$$B=\frac{1}{4}\frac{T}{\mu}, \qquad (4)$$

$$C=\frac{1}{6}\frac{T}{\mu}.$$

Reference to Eq. (2a) shows that, in our notation, Young's modulus equals 3μ when $\lambda\gg\mu$.

In order to obtain the total effect of the filler particle, it is necessary to form the strain energy function W and to integrate W throughout the volume of the rubber. Upon carrying out this operation, we obtain

$$\int_v W\,dV=\frac{T^2}{2\mu}\left\{\frac{1}{3}\left(V-\frac{4}{3}\pi a^3\right)+\frac{1}{2}\cdot\frac{4}{3}\pi a^3\right\}, \qquad (5)$$

where V is the total volume of the rubber plus that of the particle. For N particles per unit volume, the average energy per unit volume becomes

$$\bar{W}=\frac{T^2}{2\mu}\left(\frac{1}{3}+\frac{1}{6}\cdot N\cdot\frac{4}{3}\pi a^3\right)$$

$$=\frac{T^2}{2}\frac{1}{3\mu}\left(1+\frac{1}{2}\Phi\right)$$

$$=\frac{A^2M}{2}\left(1+\frac{1}{2}\Phi\right), \qquad (6)$$

where Φ is the fractional volume loading calculated on the total volume of the mix, and M is Young's modulus of the rubber matrix. In agreement with this equation, Weiss[7] and Rehner[8] have recently concluded that the energy of deformation of compounded rubber is independent of the particle size of the filler.

We now wish to determine the sum of the effects at some arbitrary point in the rubber owing to all the filler particles. We may rewrite the last member of Eq. (2a) in the following form:

$$w_0=Az, \qquad (7)$$

where z is now a coordinate referred to an arbitrary zero, located in the rubber matrix, with the Z axis parallel to the direction of stretch. We now suppose that the filler particles are distributed uniformly throughout the rubber, and that they are so far apart that their effects upon the point x, y, z are small compared to u_0, v_0, w_0. Then

$$w=+Az+\sum w_n, \qquad (8)$$

where w_n is the modification in the Z component of the displacement owing to the nth particle. We

can obtain the over-all modulus upon bringing this last equation to the form

$$w=\bar{A}z. \tag{9}$$

Substituting for w_n from Eq. (3), after transformation to the new coordinates, and replacing the summation with an integration, we find

$$\bar{A}=A\left(1-N\cdot\frac{4}{3}\pi a^3\right)$$

$$=A(1-\Phi). \tag{10}$$

The average energy $\bar{W}$ is related to the constant $\bar{A}$ by the equation

$$\bar{W}=\frac{\bar{A}^2M^*}{2}, \tag{11}$$

where M^* is Young's modulus of the compounded stock, i.e., the over-all modulus. Equation (6) gives us, however, another value for $\bar{W}$. Upon equating these two expressions, and substituting for $\bar{A}$ from (10), we find

$$\frac{\bar{A}^2M^*}{2}=\frac{A^2(1-\Phi)^2M^*}{2}=\frac{A^2M}{2}(1+\tfrac{1}{2}\Phi).$$

Cancelling and dividing through by $(1-\Phi)^2$ we find

$$M^*=M(1+2.5\Phi), \tag{12}$$

upon neglecting higher powers in Φ.

This last equation is the desired result. Its content may be expressed in words by the statement that the relative modulus (M^*/M) is directly proportional to the volume loading and is independent of particle size of the filler. The factor of proportionality, 2.5, is the same as that found by Einstein for the viscosity of a suspension.

There is some interest attached to a calculation of the stress system in the vicinity of the filler particle. The results may be written in the following form, using spherical coordinates with origin at the center of the particle and polar axis in the direction of stretch:

$$\widehat{rr}=\left\{\frac{1}{3}-(1-\cos^2\vartheta)\left(\frac{1}{3}+\frac{5}{2}\frac{a^3}{r^3}-2\frac{a^5}{r^5}\right)\right\}T,$$

$$\widehat{\vartheta\vartheta}=\left\{1-\cos^2\vartheta-(3-7\cos^2\vartheta)\frac{a^5}{r^5}\right\}T,$$

$$\widehat{\varphi\varphi}=-\frac{T}{2}(1-5\cos^2\vartheta)\frac{a^5}{r^5}, \tag{13}$$

$$\widehat{r\vartheta}=-T\sin\vartheta\cos\vartheta\left(1-\frac{5}{2}\frac{a^3}{r^3}+4\frac{a^5}{r^5}\right),$$

$$\widehat{r\varphi}=\widehat{\vartheta\varphi}=0.$$

Here $\widehat{rr}$ is the radial component of the stress acting on a plane perpendicular to the radius vector. $\widehat{\vartheta\vartheta}$ is the component, along the ϑ coordinate direction, of the stress acting on a plane perpendicular to this direction. A similar definition holds for $\widehat{\varphi\varphi}$. The remaining stress components (for example, $\widehat{r\vartheta}$) represent the radial component of the stress acting on a plane perpendicular to the ϑ coordinate direction, etc.

We are most interested in the forces tending to separate the rubber from the filler particle. These are derived from the above equations by setting $r=a$. Then

$$\widehat{rr}=-\frac{1}{2}(1-5\cos^2\vartheta)T,$$

$$\widehat{r\vartheta}=-\frac{5}{4}T\sin 2\vartheta. \tag{14}$$

From the foregoing, we see that the normal stress at the interface is a maximum at the poles of the particle, that is, when $\vartheta=0$ or 180°. At these points the stress is equal to twice the tension in the rubber matrix at a large distance from the filler particle. As ϑ increases from 0 to 90° the normal stress decreases from twice the tension in the rubber at $\vartheta=0$ to zero at $\vartheta=63°\,26'$. The normal stress then changes from tension to compression, and increases in magnitude up to $\vartheta=90°$, at which point it is equal to the tension T. The shearing component is zero both at the poles and around the equator of the particle. When ϑ goes from 0 to 90° the shearing component increases to a maximum at 45° and then decreases again to 0. The maximum shearing stress at $\vartheta=45°$ is equal to 1.25 times the tension in the rubber.

It must be emphasized that the foregoing equations are valid only for infinitely small displacements. Of course the strains in rubber in the interesting range are far from being infinitely small. However, the results just described will remain qualitatively correct for the case of finite strains. That is to say, the normal component of force at the poles will always be greater than the tension in the rubber matrix. Furthermore, the particle will always experience a com-

pression along the equatorial region, and shearing stresses at intermediate points. This, of course, is just what one would expect.

A further limitation on the preceding calculations is the fact that we have assumed the filler particles to be spherical. When this is not the case, it may be expected that the stresses tending to separate the rubber from sharp points or corners near the poles will be considerably greater than those indicated by the calculation.

III. EXPERIMENTS

Data sufficient to give an adequate test of these calculations are not available in the literature. In order to obtain such a test, we need measurements of the modulus at zero elongation of a series of stocks containing low volume loadings of various fillers, and prepared in such a way that the modulus of the rubber matrix is known. Since the effects we wish to measure are rather small (10 percent volume loading should cause only a 25 percent increase in modulus), it is necessary that the measurements be of a high degree of accuracy. The following experiments were therefore performed.

A complete formula for a gum stock was mixed. Into portions of this master batch were milled varying amounts of the fillers to be investigated. The different samples were then cured, and it was assumed that the modulus of the rubber matrix in the compounded stocks was the same as that of the gum stock cured from the same master batch when the samples were at the same state of cure. When this assumption is fulfilled, it is possible to obtain a direct check upon the validity of Eq. (12). As will be seen, however, this basic assumption was not always valid. Precautions were taken to subject the pure gum blank to milling and storage conditions identical with those which were employed for the compounded stocks.

Most of the experiments were carried out on a simple Captax stock containing 3 parts of sulfur. A few measurements were also made on a base mix containing Hepteen and 3 of sulfur with no zinc oxide. The fillers investigated were carbon black, P-33, Thermax, Kadox, XX zinc oxide, Gilder's whiting, and Catalpo clay. In some cases additional Captax was added to the carbon black stocks in order to counteract the retarding effect of this filler. Formulas are given in Table I.

The amount of filler added was checked throughout the bulk of the experiments by weighing the master batch as soon as it had been broken down upon the mill, incorporating the filler, and then weighing the completed mix again, the weight of filler added being obtained by difference.

In order to obtain the desired accuracy, special test pieces measuring $\frac{1}{4}\times\frac{1}{4}\times 24''$ were prepared. Stocks were calendered, and 13 plies were plied up to a thickness of $\frac{1}{4}''$. Strips $\frac{3}{8}''$ wide were cut from these sheets and placed edgewise in the mold. This gave an unusually large overflow and

TABLE I. Formulas.

	SLS	*SLT*	*SLU*
Blended Pale Crepe A	100	—	—
Hepteen	2	—	—
Sulfur	3	—	—
SLS	—	105	105
Gilders whiting	—	13	27
Cured 45–60–75–90′ @ 40#			

	SMN	*SMO*	*SMP*
Blended Pale Crepe A	100	—	—
Kadox	1	—	—
Laurex	3	—	—
Captax	0.5	—	—
Sulfur	3	—	—
SMN	—	107.5	107.5
Thermax	—	21	—
Channel black	—	—	21
Captax	—	—	0.2
Cured 45–60–75–90′ @ 30#			

	L
Blended Pale Crepe A	100
Kadox	1
Laurex	3
Captax	0.5
Sulfur	3
Cured 30–45′ @ 30#	

	M	
Unbroken down Pale Crepe	100	Master batch for samples *N–AB*
Kadox	1	
Laurex	3	
Captax	0.5	
Sulfur	3	

	N	*O*	*P*	*R*	*S*	*T*	*U*	*V*
M	107.5	107.5	107.5	107.5	107.5	107.5	107.5	107.5
Channel black	47.5	10	—	—	—	—	—	—
P-33	—	—	21	—	—	—	—	—
Catalpo clay	—	—	—	31	—	—	—	—
Gilders whiting	—	—	—	—	—	15	32	72
Captax	0.7	0.5	—	—	—	—	—	—

	W	*X*	*Y*	*Z*	*AA*	*AB*
M	107.5	107.5	107.5	107.5	107.5	107.5
Kadox	—	32	67	—	—	—
XX zinc oxide	—	—	—	32	67	152
Cured 45–60–75–90′ @ 30#						

resulted in complete filling of the mold and elimination of air bubbles.

Measurements of modulus were made in the following manner:

Each sample was first weighed to the nearest centigram, and then given a standard massage of 20 stretches to about 100 percent elongation. The width and thickness of the sample were then gauged in several places and the averages recorded. The length of the specimen was also measured in each case. To obtain accurate bench marks two needles were then inserted, one near

each end, and perpendicular to the long axis. The sample was then mounted in a clamp so that the protruding points of the needles rested against the scale of a meter stick. After reading the initial distance between the needle points, various loads from 0.5 to 1.5 kilograms were applied to the lower end of the test piece. After the application of each load the test piece was oscillated about its point of equilibrium and the positions of the needle points read. The resulting observations gave, therefore, a reversible stress-strain curve according to Gerke's technique.[3] After application of the highest load used in each series of measurements, the weight was removed and the length of the test piece at zero load again determined, in order to insure the absence of appreciable set.

In general, only three points were taken on the stress-strain curve of each sample, the maximum elongation varying from 10 to 30 percent. Preliminary experiments showed that a greater number of points were unnecessary for the present purpose, and also that the technique employed gave a curve with negligible hysteresis loop.

The data were treated as follows: For each measurement the percentage elongation was calculated from the measured lengths. This was divided into the corresponding load causing the elongation. The values of load divided by elongation were then plotted against elongation, and the resulting curve extrapolated to zero elongation. The resulting intercept was divided by the area of cross section of the test piece, and converted to Young's modulus at zero elongation in kg/cm². It is this value of modulus which is used throughout the subsequent discussion.

The density of each sample was calculated from the measured weight and dimensions. From the known ratio of weight of filler to weight of rubber plus curing agents (obtained on the raw mixes) and from the densities of the cured stocks, the volume loadings were calculated.

In order to obtain a reference for the state of cure of the samples, the *T*-50 test was performed on specimens cut from the cured strips.

The data obtained (density, volume loading, *T*-50, and Young's modulus) are collected in Table II. Figures following letter codes refer to times of cure, except for stock *L*. Here the first figure indicates mold cavity, the second, time of cure. Small letter (*a*) following the letter code indicates a repeat cure, made from the same mix.

TABLE II.

	Density of cured strip	Vol. % of filler 100Φ	Minus *T*-50 of cured strip	Elong. in *T*-50 test	Young's modulus @ zero elongation kg/cm²
Gum stocks:					
SLS 45	.928	—	10.8	800%	9.48
60	.930	—	15.2	800	(9.08)
75	.930	—	18.9	800	9.64
SMN 45	.940	—	12.8	800	13.76
60	.941	—	16.1	800	13.10
75	.940	—	17.7	800	12.43
90	.941	—	20.1	800	12.99
SMN(*a*) 45	—	—	17.3	800	13.06
60	—	—	19.8	800	12.78
75	—	—	22.1	800	12.87
90	—	—	24.6	800	12.28
L-1 30	.982	—	−0.5	800	12.72
L-3 30	.987	—	0.9	800	12.56
L-5 30	.982	—	−0.3	800	12.56
L-1 45	.983	—	10.0	800	14.28
L-3 45	.986	—	9.8	800	14.17
L-5 45	.989	—	8.9	800	14.22
S-45	.973	—	10.2	800	13.61
60	.972	—	13.8	800	13.97
75	.984	—	16.2	800	13.59
90	.987	—	19.5	800	13.02
W 45	.984	—	11.8	800	14.28
60	.988	—	15.3	800	14.40
75	.979	—	18.8	800	13.61
90	.984	—	21.3	800	12.85
Carbon black:					
O 45	1.024	6.4	12.8	350%	18.32
60	1.023	6.4	16.9	350	18.93
60	1.031	6 4	17.5	350	17.57
75	1.030	6.4	*B*	350	(16.92)
90	1.037	6.4	29.7	350	16.83
SMP 45	1.015	9.6	5.3	350	19.56
60	1.017	9.6	12.6	350	19.70
75	1.018	9.6	15.0	350	19.70
90	1.018	9.6	17.2	350	19.10
SMP(*a*) 45	—	9.6	—	350	20.7
60	—	9.6	—	350	21.4
75	—	9.6	—	350	19.87
90	—	9.6	—	350	18.91
N 45	1.109	23.5	5.1	350	44.1
60	1.111	23.5	9.8	350	44.5
60	1.108	23.5	7.2	350	42.1
75	1.110	23.5	15.8	350	(36.0)
90	1.116	23.5	17.2	350	42.7
P-33:					
P 45	1.068	10.1	9.8	500%	17.37
60	1.077	10.1	15.9	500	17.52
60	1.063	10.1	16.8	500	17.18
75	1.070	10.1	25.1	500	(15.52)
90	1.069	10.1	21.9	500	16.00

TABLE II.—*Continued.*

	Density of cured strip	Vol. % of filler 100Φ	Minus T-50 of cured strip	Elong. in T-50 test	Young's modulus @ zero elongation kg/cm²
Thermax:					
SMO 45	1.022	9.0	12.3	650%	15.92
60	1.023	9.0	17.4	650	15.39
75	1.022	9.0	19.6	650	15.01
90	1.023	9.0	22.7	650	14.78
SMO(a) 45	—	9.0	10.6	650	16.22
60	—	9.0	16.2	650	15.27
75	—	9.0	19.1	650	15.21
90	—	9.0	23.0	650	14.50
Kadox:					
X 45	1.191	5.9	11.3	500%	18.08
60	1.197	5.9	17.8	500	19.42
75	1.188	5.9	22.1	500	19.73
90	1.191	5.9	25.6	500	20.2
Y 45	1.417	10.6	9.4	500	21.5
60	1.420	10.6	14.5	500	22.9
75	1.410	10.6	19.3	500	24.0
90	1.415	10.6	23.2	500	25.7
XX zinc oxide:					
Z 45	1.211	5.4	4.2	500%	16.91
60	1.197	5.4	9.9	500	18.43
75	1.193	5.4	14.8	500	19.48
90	1.197	5.4	19.3	500	19.67
AA 45	1.413	10.4	1.9	500	20.4
60	1.409	10.4	7.2	500	22.1
75	1.410	10.4	11.6	500	23.4
90	1.419	10.4	16.2	500	24.9
AB 45	1.873	20.9	−1.5	500	28.4
60	1.872	20.9	3.6	500	30.2
75	1.865	20.9	7.2	500	32.1
90	1.872	20.9	12.0	500	34.1
Gilders whiting:					
SLT 45	1.001	4.1	13.2	650%	10.29
T 45	1.067	3.8	9.8	650	16.42
60	1.078	3.8	16.7	650	16.55
75	1.063	3.8	18.9	650	15.95
90	1.069	3.8	20.1	650	15.37
SLU 60	1.072	8.3	15.4	500%	11.77
75	1.071	8.3	16.4	500	11.97
U 45	1.141	10.3	9.1	500	18.68
60	1.134	10.3	17.2	500	18.62
75	1.137	10.3	21.2	500	18.50
90	1.144	10.3	23.0	500	17.93
V 45	1.295	20.6	6.3	500	24.8
60	1.301	20.6	15.4	500	25.1
75	1.300	20.6	17.6	500	24.9
90	1.298	20.6	20.5	500	23.2
Catalpo clay:					
R 45	1.118	10.4	−2.8	500	19.37
60	1.113	10.4	5.4	500	21.25
75	1.128	10.4	11.5	500	21.15
90	1.126	10.4	17.0	500	21.7

Data in parentheses were omitted when considering the results. The 60′ cure of *SLS* and the 75′ cure of *N*, *O*, and *P* gave discordant moduli, possibly because of irregular curing conditions.

IV. DISCUSSION OF RESULTS

Before proceeding to an analysis of the results, it is desirable to obtain some idea of the accuracy of these measurements. This may be obtained from the data for samples *L*-30 and *L*-45 (Table II). These are gum stocks and were cured with the object of determining whether or not there is any difference in curing rate between the cavities 1, 3, and 5 of the mold. The fact that the two sets of three measurements agree among themselves shows that the curing does not depend upon the cavity of the mold. The maximum variation within each of these sets of three measurements is about 1 percent. It is believed that the individual measurements of Young's modulus, listed in Table IV, all have about this same accuracy.

Comparison of stocks *S* and *W*, however, shows that variations in modulus of 4 to 5 percent may occur as a result of different curing conditions. These two stocks were prepared from the same mix, but cured on different days. Variations of this type were not controlled in these experiments: They therefore represent the limit of accuracy of the absolute values recorded. It seems reasonable, however, to expect relative accuracy greater than this, when comparing samples cured in the same load.

It is necessary to know the modulus of the matrix in the compounded stocks, in order to check the theoretical result contained in Eq. (12). It was intended to measure the moduli for each mix over a range of cures, and plot these values against the corresponding T-50. It should then be a legitimate procedure to assume that the modulus of the matrix in the compounded stock, for a particular point of the modulus-T-50 curve, is equal to the modulus of the gum stock at the corresponding point of its modulus-T-50 curve. This procedure proved to be impracticable for the following reasons:

Because of the varying characteristics of the compounds studied, it was not possible to obtain significant T-50 values at a single elongation. Reference to Table II will show that the elongations varied from 350 percent for the highly loaded stocks, to 800 percent for the gum stocks. It seems unlikely that the T-50 values are comparable throughout this wide range of elongation.

A more serious factor in precluding the use of T-50 as a reference for state of cure lies in the fact that the modulus-T-50 curves differed greatly in shape, depending on the filler used.

The gum stocks showed a fairly pronounced maximum. The carbon black stock, however, was nearly flat throughout a large part of the curve, and the compound containing Kadox showed a steadily increasing modulus with decreasing T-50. Obviously it is impossible to pick from these curves any satisfactory reference point.

Another difficulty lies in the fact that two different curves were obtained for stocks S and W. These were made from the same mix, but cured on different days. The fact that the differences in modulus shown by these two stocks are not reflected in the T-50 test means that some other factor enters into the results.

In default of any better procedure, it was decided to assume arbitrarily that the modulus in the compounded stock is equal to the modulus of the gum stock which had the same curing time. Whenever a gum stock was included in the press load its modulus was used in calculating the relative modulus (M^*/M). In those cases in which no gum stock was in the mold, the average for stocks S and W was set equal to M, the modulus of the matrix, for stocks N to AB.

This procedure is arbitrary and in some cases definitely wrong—for example, the stocks containing zinc oxide. However, the conclusions to be drawn from the data do not depend upon this method of calculation, but would follow from any of a number of other methods which have been employed.

The values so obtained are summarized in Table III, together with the average relative

TABLE III. M^*/M.

Code	Filler	100Φ	45′	60′	75′	90′	Observed Av.	Calc.
O	Carbon black	6.4	1.31	1.34	1.25	1.30	1.30	1.16
SMP		9.6	1.42	1.50	1.58	1.47	1.54	1.24
SMP(a)		9.6	1.59	1.68	1.54	1.54		
N		23.5	3.16	3.14	2.97	3.30	3.17	1.59
P	P-33	10.1	1.25	1.24	1.21	1.24	1.24	1.25
SMO	Thermax	9.0	1.16	1.17	1.21	1.14	1.19	1.22
SMO(a)		9.0	1.24	1.20	1.18	1.18		
X	Kadox	5.9	1.27	1.35	1.45	1.57	1.41	1.15
Y		10.6	1.51	1.59	1.76	2.00	1.72	1.26
Z	XX zinc oxide	5.4	1.21	1.30	1.43	1.52	1.37	1.13
AA		10.4	1.47	1.56	1.72	1.92	1.68	1.26
AB		20.9	2.04	2.13	2.36	2.64	2.29	1.52
SLT	Gilders whiting	4.1	1.09	—	—	—	1.09	1.10
T		3.8	1.18	1.17	1.17	1.19	1.18	1.09
SLU		8.3	—	1.23	1.24	—	1.24	1.21
U		10.3	1.34	1.31	1.36	1.39	1.35	1.26
V		20.6	1.78	1.77	1.83	1.79	1.79	1.51
R	Catalpo clay	10.4	1.42	1.52	1.56	1.67	1.54	1.26

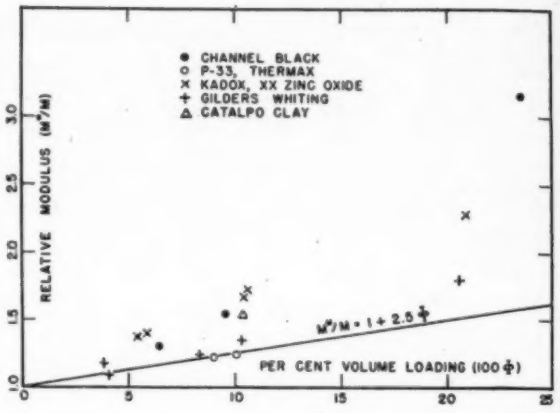

FIG. 1.

modulus for all cures of each mix, and the calculated value of this quantity. Relative moduli, averaged over all cures, are plotted against Φ in Fig. 1. Examination of these data shows that in no case (with the exception of Kadox and XX zinc oxide) is there any pronounced variation in relative modulus as cure progresses. This may be taken as justification of the validity of the procedure employed, for fillers other than zinc oxide.

It is at once apparent that there are many discrepancies between the observed and calculated values. In order to obtain information from these measurements, it will be desirable to examine each filler separately.

Carbon Black

The values observed for relative modulus are markedly greater than the calculated values. In order to account for these discrepancies it is only necessary to recall that carbon black is generally recognized to be flocculated in rubber.[4–5] When flocculated, the filler particles are, on the average, much closer together than would be the case for perfect dispersion. It is therefore apparent that the assumptions underlying Eq. (12) are not fulfilled. Thus, if the carbon particles are far apart from each other within the rubber, their effects upon the displacement when the rubber is stretched will be additive. If, however, the particles are close together, their effects on the displacement in the rubber will be far from additive. It is physically obvious that, when the particles are near together, the increase in modulus will be greater than when they are far apart. Suppose, for example, all of the particles

in a dilute mix were placed touching each other, and in lines parallel to the direction of stretch. Assuming complete adhesion and rigid particles, it is apparent that the over-all structure would also be rigid, the effect of the contacting particles being similar to a rigid bar immersed in the elastic rubber. Another factor that may be of importance is our neglect of the molecular structure of the rubber, since the carbon black particle is not large compared to this structure.

Soft Blacks (P-33, Thermax)

These fillers yield values for relative modulus substantially in agreement with those calculated from Eq. (12). It appears that soft blacks are well dispersed in rubber, and that, at small elongations, there is good adhesion between the matrix and the filler.

Zinc Oxides (Kadox and XX Zinc Oxide)

These fillers did not show conformity to Eq. (12) according to these experiments. Microscopic studies have shown that zinc oxide is well dispersed in rubber. The relative moduli, however, are abnormally high. Because of the microscopic evidence this cannot be ascribed to flocculation of the filler. It may be in part owing to the acicular shape of the ultimate particles of zinc oxide (see catalpo clay, below) but this cannot account for the entire effect produced. It is also noteworthy that these stocks do not show any reversion (i.e., decrease in modulus in the longer cures) throughout the range of cures employed in these experiments. This behavior is distinct from all other samples studied in this series. It seems fair to assume that the abnormalities in modulus shown by zinc oxide are caused by the effect of this filler upon the type of cure of the rubber matrix, and we may conclude from the present results that the high modulus of zinc oxide stocks is owing to a pronounced stiffening of the rubber matrix, but that in other respects the filler is normal and well dispersed. This interpretation requires the assumption that in the most extreme case (stock *AB*, 90′ cure, 20 percent by volume XX zinc oxide) the modulus of the matrix is 50–60 percent greater than that of the pure gum blank. This does not seem improbable.

Whiting

Relative moduli on Monex stocks are in complete agreement with the calculations, but in the Captax stocks, relative moduli are higher than the calculated values by an amount which appears to be greater than the experimental error. The cause of this discrepancy is not known. It should be pointed out that at volume loadings as high as 20 percent discrepancies may be expected to occur, since at these concentrations the suspension can no longer be considered dilute. It may be concluded that whiting is well dispersed in rubber.

Catalpo Clay

The relative modulus is abnormally high. This behavior is undoubtedly to be interpreted as being caused by the pronounced acicular shape of the clay particles. The strips on which Young's moduli were determined were made from a calendered stock and the direction of stretch coincided with that of the calender grain. It is well known that calendering a stock containing an anisotropic filler results in alignment of the filler particles in the direction of the calender grain. Because of this, the effective volume loading is greater in this direction than that calculated on the assumption of spherical particles.[6] The increase in modulus is therefore greater than expected. Other measurements on Catalpo stocks in which there was little if any calender grain have shown agreement with Eq. (12).

In conclusion it can be stated that Eq. (12) gives a satisfactory representation of the increase in modulus of a rubber compound due to addition of a filler, whenever certain idealized conditions are approximately fulfilled. These conditions are caused by the simplifying assumptions made in carrying out the calculations. According to these assumptions, the filler particles must be spherical, or nearly so, and there must be complete adhesion between the rubber and the filler. The filler is assumed to be completely and uniformly dispersed, and at a volume loading small enough to justify neglect of effects due to pairs of particles. Throughout the calculations the rubber matrix has been treated as a continuous medium. It is possible that extremely small filler particles might require consideration of the molecular structure of the rubber hydrocarbon.

Equation (12) is thus an idealized limiting law. As illustrated in the discussion of the experimental results here presented, departures from this law may lead to conclusions on the dispersion of the filler and on the state of cure of the rubber matrix.

Dependence of reinforcement on particle size of filler is worthy of further discussion. Throughout the majority of the literature on the subject, it has been assumed that decreasing particle size means increasing reinforcement. The calculations reported in this paper show that, in the ideal case, there can be no primary relation between the particle size of filler and reinforcement, as judged by modulus at low elongations. Experiments other than those here reported show that carbon black gives greater increases in modulus than other commercial fillers, and that, for a given volume loading and time of cure, substantially all other commercial fillers show much the same modulus at low elongations. Cotton[9] and others have prepared sheets of rubber containing rigid inclusions several millimeters in diameter. These inclusions cause approximately the same increase in modulus as do fillers with particle diameter of the order of 1 micron. This similarity between microscopic particles and rigid inclusions some 1000–10,000 times larger is, of course, in agreement with Eq. (12). If there were any functional dependence of reinforcement on particle size it could only become apparent at particle sizes well under 1 micron. It therefore appears that theory and experiment agree in the conclusion that there is no direct relationship between reinforcement and particle size of filler.

It is entirely possible, however, that particle size of filler may indirectly affect the phenomena of reinforcement. This can occur through either of two mechanisms. Fillers which tend to flocculate in rubber may do so to a greater or less extent. The extent of flocculation may be determined in part by the particle size of the filler. Alternatively, some fillers affect the state of cure or the type of cure of the rubber matrix. The magnitude of these effects may well depend upon the particle size of such fillters. In addition, as noted above, when the particle size becomes so small that the rubber can no longer be treated as a continuum, other effects may require attention. These effects might appear whenever particle size is of the same order of magnitude as, or smaller than, the molecular dimensions of the rubber.

ACKNOWLEDGMENT

It is a pleasure to express my indebtedness to Dr. M. Mooney of these laboratories for his continued interest and helpful advice in carrying out the calculations reported in this paper.

SUMMARY

1. Analysis shows that, subject to certain limitations, the modulus of a loaded stock (M^*) depends upon the modulus of the rubber matrix (M), according to the equation

$$M^* = M(1+2.5\Phi),$$

where 100Φ is the volume percent of filler.

When these limitations are fulfilled, the effect of compounding upon modulus is therefore independent of the particle size of the filler.

The assumptions upon which this equation is founded are as follows: (1) The filler particles are spherical, (2) there is complete adhesion between rubber and filler, (3) the elongation is small, (4) the filler is completely dispersed, (5) the volume loading is small, (6) the filler particles are sufficiently large that the molecular structure of the rubber may be neglected.

2. The stresses about a filler particle have been derived mathematically.

3. Experimental data check the calculations for the following fillers: P-33, Thermax, and whiting. Catalpo clay presents some anomalies because of its acicular particles.

4. Carbon black does not conform to the calculations. This is attributed to the fact that it is strongly flocculated in rubber.

5. Zinc oxide (Kadox or XX zinc oxide), which should conform, because it is well dispersed in rubber, causes abnormally large increases in modulus, presumably because of alteration of the type of cure and consequent alteration of the modulus of the rubber matrix.

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Some Low Temperature Properties of Elastomers*

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A modification of the apparatus employed in measuring the Young's modulus of elastomers at low temperatures is described. The changes made in the apparatus permit the use of a simplified technique which can be adapted to routine testing procedure. The effects of various softeners on the low temperature bending moduli and the brittle point temperatures of stocks based on four butadiene-acrylonitrile (B/A) type copolymers are given. It is shown that the softeners tested have the same relative effects in all four types and that a wide variation in low temperature properties is imparted to the stocks by the different softeners. Bending modulus curves and brittle point temperatures are given for typical test stocks based on Thiokol FA, and "mass" and "emulsion" polymerized polybutadiene. It is shown that continued exposure to low temperature affects the Young's modulus of some but not all typical vulcanizates. Data are presented showing this effect on an uncured Hevea gum stock held at 0°C. Certain softeners have been found to induce time effects in one of the B/A type stocks, which exhibits no crystallization, and hence no progressive stiffening in the absence of the given softeners. A method for measuring and evaluating creep under dead load at low temperatures is presented. Accompanying data indicate that in the case of those stocks tested, the creep constant defined reaches a maximum at a definite temperature which is a characteristic of the given stock.

INTRODUCTION

APPARATUS and techniques for the determination of Young's modulus of elastomers at low temperatures have been described in a previous publication.[1] The objects of the work described in the present report were (1) to extend the Young's modulus measurements to materials not previously studied, and (2) to present some preliminary data on creep phenomena at low temperatures. Improvements have been made in the apparatus since the original description was published and the test technique previously described has been simplified. A photograph of the present modified, assembled equipment is shown in Fig. 1. A schematic sketch, showing details of the various mechanisms, is given in Fig. 2.

It is well known that high-polymeric materials, such as Hevea rubber and most of the synthetic "rubbers," under conditions of low strain, exhibit reversible, delayed elasticity. A result of this effect is that the application of a given, constant force (in bending a sample piece, for example) produces, not a fixed deflection, but rather one which depends on the duration of the force application. The total strain at any point in the sample, resulting from such force application, can be considered to be made up of two parts: one an instantaneous deflection independent of time and the other a creep strain dependent on time. It has been proposed[2] that such effects, together with associated stress relaxation effects, be referred to as primary creep phenomena.

The materials referred to above exhibit further creep effects under conditions of large strain, high temperatures, and extended times. Such effects result in plastic flow (under some conditions ultimately in failure) and are termed secondary creep phenomena. Inasmuch as a separation of primary and secondary creep is

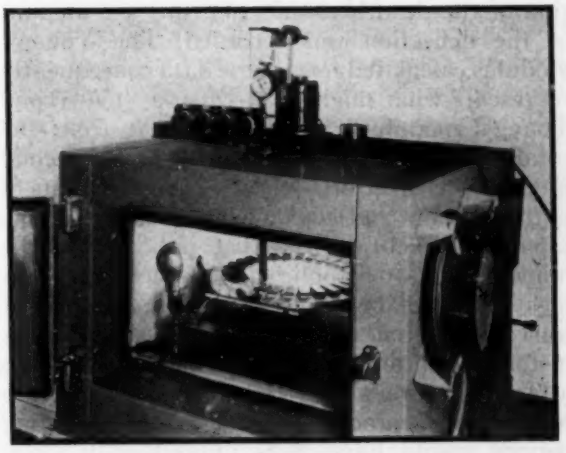

FIG. 1. Photograph of apparatus.

* Presented on June 24, 1944 before the Inaugural Meeting of the Division of High-Polymer Physics of the American Physical Society at Rochester, New York.

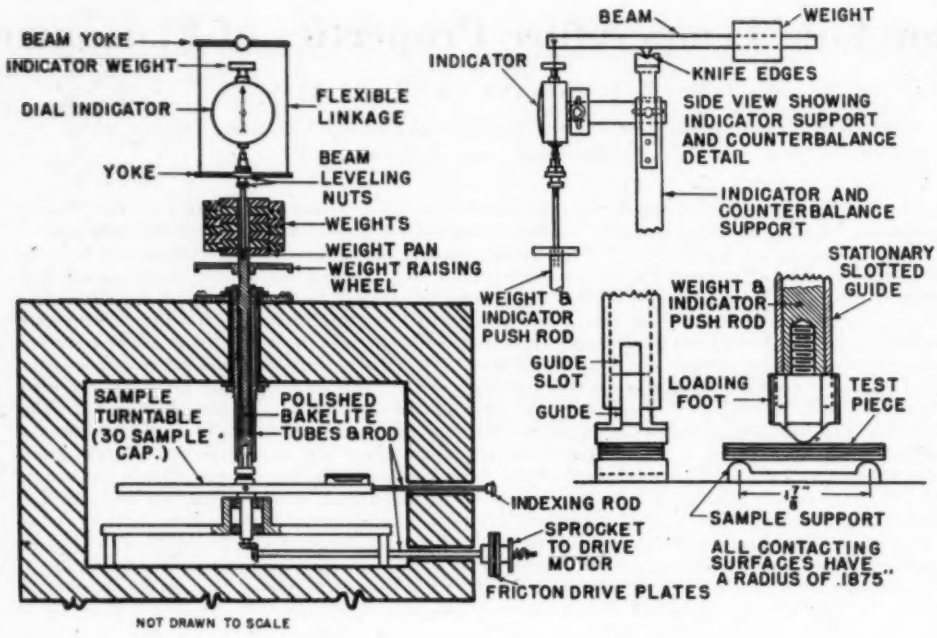

FIG. 2. Schematic sketch of apparatus.

extremely difficult at best, all observations reported in this work were made under such conditions that secondary creep was not present (or negligibly small). The data obtained can thus be interpreted in the light of primary creep theories alone.

MODULUS MEASUREMENTS

In order to obtain useful and reproducible data on the bending modulus of Hevea and other elastomers, employing the apparatus shown, it was found expedient to allow a uniform time of ten seconds to elapse between the time of application of the dead load and the time the amount of the deflection was recorded. The Young's modulus calculated from these data consequently represents what might be termed a "ten-second Young's modulus" to distinguish it from the total and instantaneous moduli. The ten-second interval was arbitrarily chosen in the interests of both accuracy and convenience. Because of the rapid movement of the dial indicator needle immediately after application of the load, readings could not be obtained accurately until at least five to ten seconds had elapsed. In most instances motion of the dial indicator needle after ten seconds was slow enough to ensure reasonable accuracy in reading. Longer loading periods would have been unnecessarily time-consuming.

In the apparatus, as originally designed, the loading mechanism (particularly the tubes and rods which extend through the walls of the cold chamber) was made of a phenol-formaldehyde resin. This material was selected to reduce transmission of heat and also to reduce the initial dead load on the sample. In spite of these precautions, the initial load totalled 368 grams. In order to keep the dead load deflection small at the higher temperatures, it was necessary to employ fairly thick test pieces (approximately $\frac{1}{2}$ inch), particularly in the case of soft, gum type stocks. At low temperatures, however, excessively high loads were required to produce reasonable deflections on such thick samples. To avoid this difficulty, two samples of each compound under investigation were placed in the unit during each test run. Load-deflection observations were made on the thick samples at the higher temperatures and on the thin samples at the lower temperatures. Although this method yielded quite satisfactory results, the capacity of the unit was thereby reduced. Furthermore, interpretation of low temperature creep data would have been considerably complicated by the existence of this high initial load. The counterbalance, shown in Fig. 2, was subsequently devised and adjusted to produce an initial load of 55 grams. It was not found feasible to reduce this initial load to zero, since experience

indicated that a small amount of stress was necessary to overcome the slight tendency of some of the samples to warp or twist as the temperature of the test chamber varied. The effect of this change in initial load on the measured modulus is small, as can be seen from typical data shown in Fig. 3. These data were obtained in the manner previously described,[1] except as noted on Fig. 3.

Corrections for indentation of sample and compression of loading rod were found to be a necessary part of the originally described technique because of the thick samples and relatively high loads employed. Introduction of the counterbalanced system eliminated the need for employing thick samples; hence the indentation corrections (formerly important at the higher temperatures) became small and negligible. Since the absolute values of the Young's moduli at extremely high values are of little commercial significance, the correction for compression of loading rod (important only at high values of moduli) was also considered unnecessary and was dropped when the counterbalance was installed. The data shown in Figs. 4 to 9, inclusive, were obtained before the counterbalance was installed and hence include all corrections described in the early technique. The data shown in the remaining figures were obtained on the counterbalanced apparatus and are not corrected either for indentation of sample or compression of loading rod. A comparison of Figs. 5 and 12 shows the effect of omitting these complicating corrections from data obtained with the counterbalanced system. It can be seen that the absolute values of Young's modulus obtained by the two techniques agree closely except at low temperatures where the moduli are so high as to be of little or no practical value.

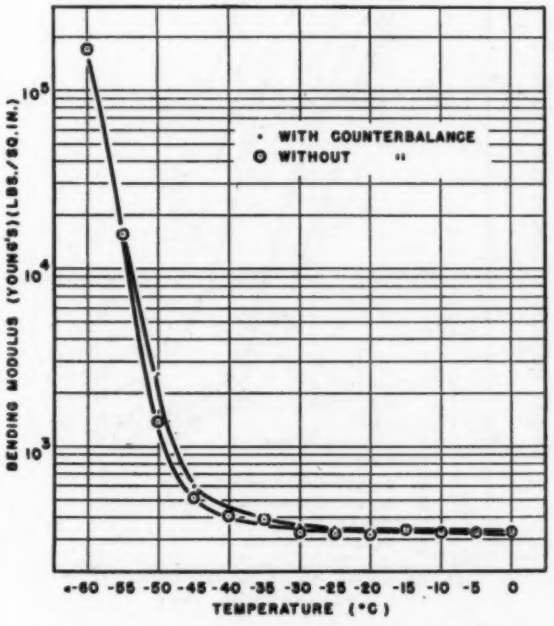

FIG. 3. Effect of counterbalance on bending modulus values for Hevea stock *A*.

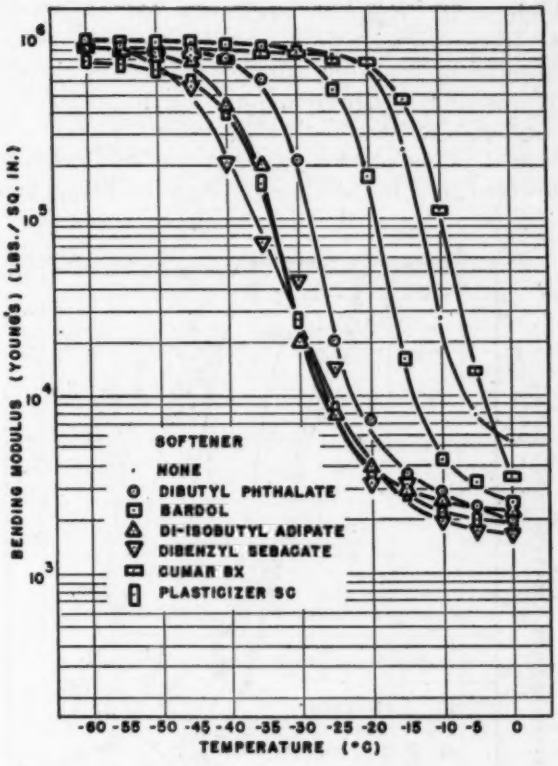

FIG. 4. Young's modulus as a function of temperatures; *B/A* type 1 stocks.

Unless specifically otherwise mentioned, all modulus data reported in this work were taken under conditions such that crystallization effects (resulting from exposure to low temperatures) were negligibly small. The modulus changes observed are hence attributable to pure second-order transition phenomena, although it should be remembered that some of the materials might ultimately have shown further stiffening as a result of crystallization, if the tests had been continued over longer periods of time.

The low temperature characteristics of stocks based on synthetic polymers depend not only on the chemical composition and physical nature of the polymer itself but also on the amount and nature of the pigments added. Data on the

change in Young's modulus with change in temperature have previously been reported for a number of synthetic rubbers as well as Hevea.[1] It was shown that compounds having better low temperature stiffening characteristics were obtained as the styrene content was progressively lowered in a butadiene-styrene type copolymer.

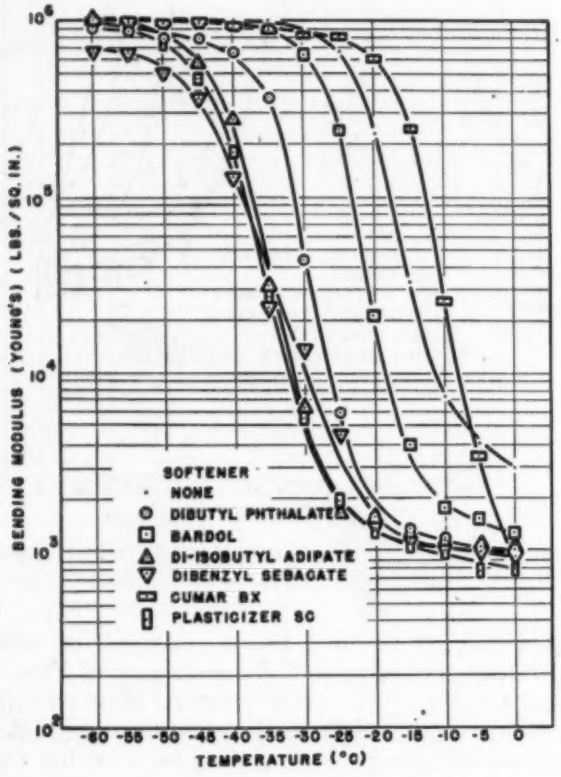

FIG. 5. Young's modulus as a function of temperature; *B/A* type 2 stocks.

A similar study has now been made with compounds based on the butadiene-acrylonitrile (*B/A*) type copolymer. Although not strictly alike in all respects (because of slight changes in the polymerization process), the major difference in the four elastomers tested is the variation in acrylonitrile content. The acrylonitrile content decreases in the order *B/A* type 1, 2, 3, and 4. The effects of several typical softeners on the low temperature stiffening characteristics of compounds based on these were also studied. The formulae of the stocks studied are shown in Table I. The Young's modulus (measured at the usual 10 seconds) *vs.* temperature curves obtained are shown in Figs. 4–7.

Brittle point temperatures, measured by a modification of the method of Selker, Winspear, and Kemp,[3] were determined on the same compounds. The results obtained are given in Table II.

TABLE I. General stock formulae (Figs. 4–7).

Polymer (as indicated)	100	pts. by wt.
Softener (as indicated)	20	
SRF black	70	
Zinc oxide	3	
Sulphur	2.5	
Benzothiazyl disulfide	1.0	

By both modulus and brittleness types of test, it can be seen that improved low temperature characteristics are progressively imparted to the *B/A* type copolymer as the amount of acrylonitrile present is reduced. Both tests also indicate that Cumar BX, though effective as a softener at normal temperatures, stiffens rather than softens the compounds at low temperatures. Beyond this qualitative agreement there is little correlation between the results obtained by the two methods. For example, in Table III are listed the moduli of the several stocks tested, at the brittle point temperature of each. These data indicate that some of the compounds become brittle (under the given conditions of

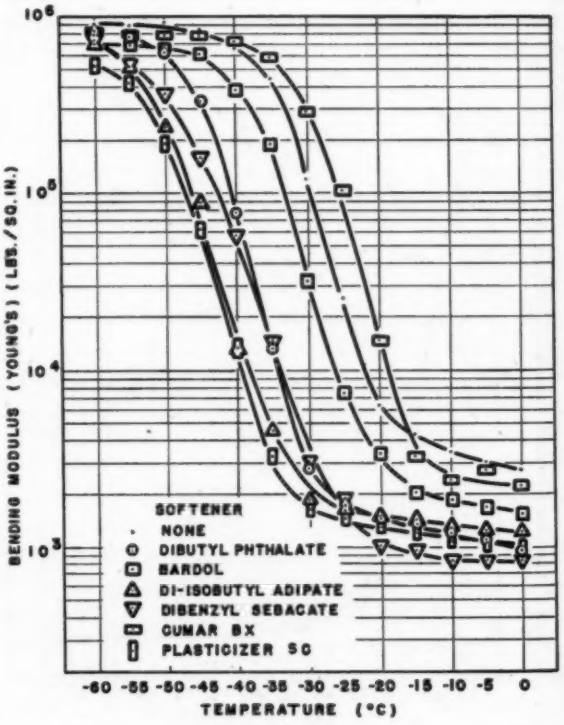

FIG. 6. Young's modulus as a function of temperature; *B/A* type 3 stocks.

TABLE II. Brittle point temperatures (°C)—*B/A* type compounds.

Copolymer type	1	2	3	4
Softener				
None	−17	−27	−41	−56
Dibutyl phthalate	−26	−34	−44	−55
Bardol	−22	−26	−38	−55
Di-isobutyl adipate	−23	−34	−44	−56
Dibenzyl sebacate	−37	−43	−55	−63
Cumar BX	−8	−16	−36	−47
Plasticizer SC	−32	−40	−49	−60

TABLE III. Modulus (in lb./sq. in.) at the brittle point temperature of each compound—*B/A* type stocks.

Copolymer type	1	2	3	4
Softener				
None	450,000	780,000	730,000	675,000
Dibutyl phthalate	36,000	260,000	275,000	325,000
Bardol	320,000	340,000	315,000	550,000
Di-isobutyl adipate	5,300	27,000	50,000	85,000
Dibenzyl sebacate	125,000	260,000	550,000	200,000 (est.)
Cumar BX	50,000	340,000	630,000	510,000
Plasticizer SC	51,000	180,000	160,000	200,000

impact velocity) even though their moduli, measured under nearly static conditions, remain reasonably low. On the other hand, the static moduli of some of the compounds are seen to be extremely high at their respective brittle point temperatures. Inasmuch as the dynamic is nearly always higher than the static modulus, the moduli of the stocks tested (under almost any set of conditions to which rubberlike materials are subjected in service) would be even higher than those tabulated. The moduli of stocks employed as vibration dampers, motor supports, diaphragms, etc., range from 300 to approximately 3000 lb./sq. in. at normal temperatures. It is doubted that a compound having a static modulus much greater than 10,000 lb./sq. in. would be of much value as a rubberlike material in normal service. Hence this value is tentatively considered to be the maximum allowable modulus for rubberlike serviceability. The temperatures at which the several compounds tested attain a modulus of 10,000 lb./sq. in. are shown in Table IV. It will be observed that these temperatures are considerably higher than the corresponding brittle point temperatures given in Table II. It is also interesting to note that, at the concentrations studied, only three of the softeners tested appreciably affected the brittle point temperatures of the *B/A* type 4 series while all had a large effect on the brittle point temperatures of the *B/A* type 1 series. As

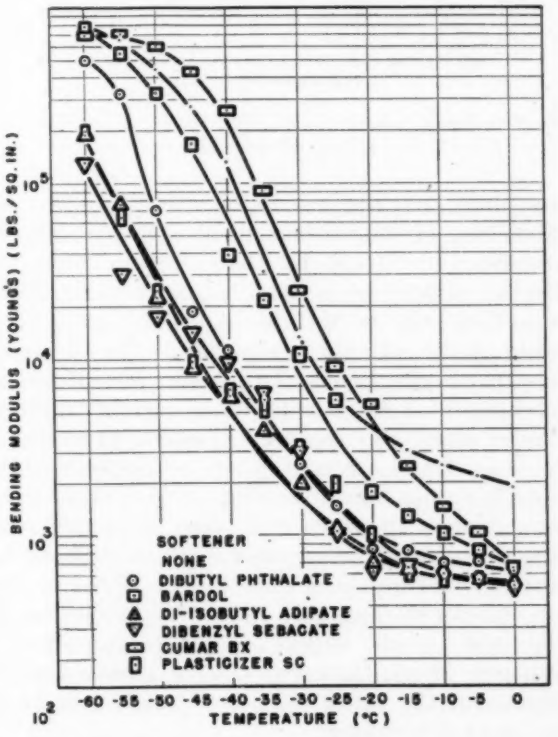

FIG. 7. Young's modulus as a function of temperature; *B/A* type 4 stocks.

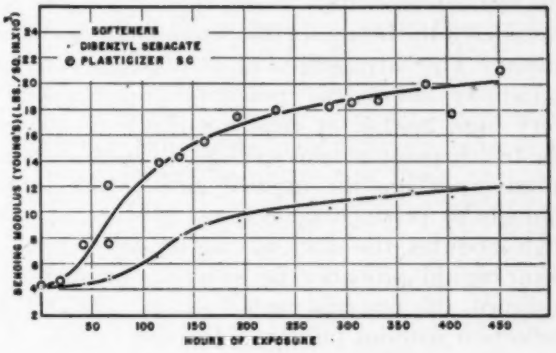

FIG. 8. Time effect on *B/A* type 4 stocks at −35°C.

TABLE IV. Temperature (°C) at which modulus is 10,000 lb./sq. in.—*B/A* type stocks.

Copolymer type	1	2	3	4
Softener				
None	−7	−11	−22	−28
Dibutyl phthalate	−23	−26	−34	−40
Bardol	−14	−19	−26	−31
Di-isobutyl adipate	−27	−31	−38	−44
Dibenzyl sebacate	−26	−30	−34	−42
Cumar BX	−4	−8	−19	−25
Plasticizer SC	−25	−32	−39	−45

judged by modulus tests, however, the effectiveness of the softeners was nearly the same in all four series of compounds.

Of two compounds (both having brittle point temperatures below the anticipated minimum temperature to which they might be subjected in service) the one having the lower modulus at the latter temperature would unquestionably be considered the better for low temperature serviceability. The advantages of compounds having extremely low brittle point temperatures but very high moduli at temperatures even above the brittle point are not so clear. In applications, however, where the applied stresses are large enough to produce deflections in spite of the high modulus, the stock having the lower brittle point would probably be selected. In such an instance, the material would survive the initial deflection without failure and would rapidly increase in temperature (and hence become more serviceable) as a result of subsequent deflections.

The data illustrate quite clearly the desirability of measuring both properties in evaluating the low temperature serviceability of a compound.

Periodic checks are made during all test runs to make certain that crystallization stiffening is not contributing to the modulus changes being observed. A slight tendency toward progressive stiffening, with continued exposure to low temperatures, was noted during the run on the *B/A* type 4 series of compounds. A further study of this series was hence made.

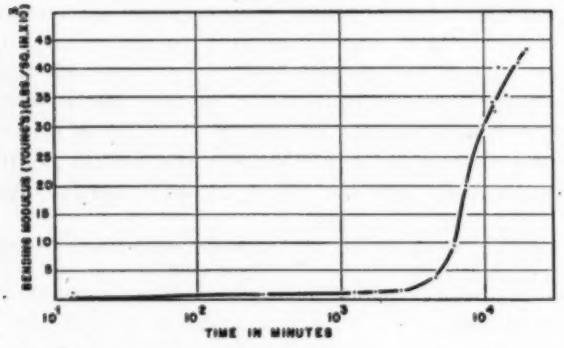

FIG. 9. Time effect on uncured Hevea stock *B* at 0°C.

The seven *B/A* type 4 stocks were placed in the cold chamber and held at −35°C for a period of 452 hours. Two of the seven exhibited a marked progressive stiffening, while the others showed none whatever up to the conclusion of the test. The modulus changes observed are shown in Fig. 8.

The observed increase in modulus is of a lower order of magnitude than that exhibited by Neoprene GN (GR-M) or unvulcanized Hevea

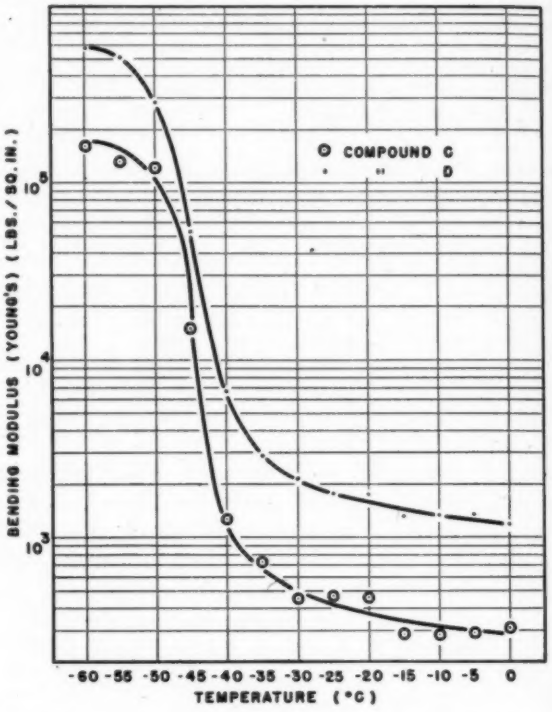

FIG. 10. Young's modulus as a function of temperature—Thiokol FA stocks.

and may be the result of crystallization or hardening of the softener itself. It has also been suggested by Mr. R. H. Taylor* of the National Bureau of Standards that this particular stiffening effect may be the result of decreasing solubility of the softener in the polymer as the temperature is decreased. If this were the case, the modulus of a stock containing such a softener should, after long exposure, approach the modulus of a similar stock containing no softener. The tests have not been extended for periods of time long enough to prove this point. However, the fact that the modulus of the stock containing no softener had not been exceeded by either of the two stocks in question, up to the conclusion of the test, lends support to this hypothesis. Whether or not these two softeners have similar effects on the other *B/A* type copolymers has not been determined.

* In private conversation, during discussions on standardization of test methods.

The effect of continued exposure to a temperature of 0°C on the bending modulus of a compound having a Hevea rubber base is shown in Fig. 9. The formula of this compound is given in Table V. Only the unvulcanized sample of

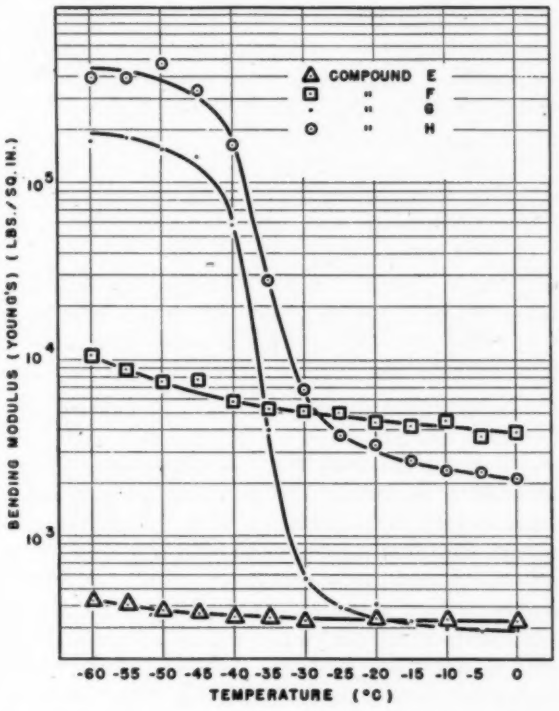

FIG. 11. Young's modulus as a function of temperature—emulsion and mass polymerized polybutadiene.

Hevea exhibited this effect up to the conclusion of this test. Samples cured 40 to 80 minutes at 270°F (the latter corresponding to a technical "optimum" cure) showed no observable progressive stiffening in this test. A comparison of Figs. 8 and 9 illustrates the difference (mentioned earlier) in the magnitudes of the effect attributable to crystallization of the elastomer itself and that resulting from the use of a particular softener in a base elastomer which, in the absence of the softener, shows no crystallization stiffening.

Thiokol FA, like Neoprene GN and unvulcanized Hevea, exhibits pronounced time-stiffening effects. Consequently, special precautions had to be observed, in obtaining Young's modulus *vs.* temperature data, to make certain that the modulus changes observed were caused entirely by second-order transition effects. The results of tests conducted under such conditions are shown in Fig. 10 for typical "gum" and SRF (semi-reinforcing furnace) black type stocks. The formulae of the stocks tested, together with brittle point temperatures, are shown in Table V. No attempt was made to evaluate the crystallization stiffening effect in the case of these two stocks, though indications were that it would be quite pronounced.

The effect of temperatures on the ten-second Young's modulus of polybutadiene compounds has been reported previously.[1] Although not specifically denoted as such at the time, the polymer employed then was made by an emulsion polymerization process. Since these results were published, a similar study was made of compounds based on mass (sodium) polymerized polybutadiene. The formulae of the compounds tested are the same as those previously employed and are given in Table V. Brittle point temperatures are also given in Table V. The modulus *vs.* temperature data obtained, given in Fig. 11, show that the two methods of polymerization produce polymers having radically different low temperature stiffening characteristics. Chemical analyses indicate[4] that the molecular structure of a polymer is affected by a change in the

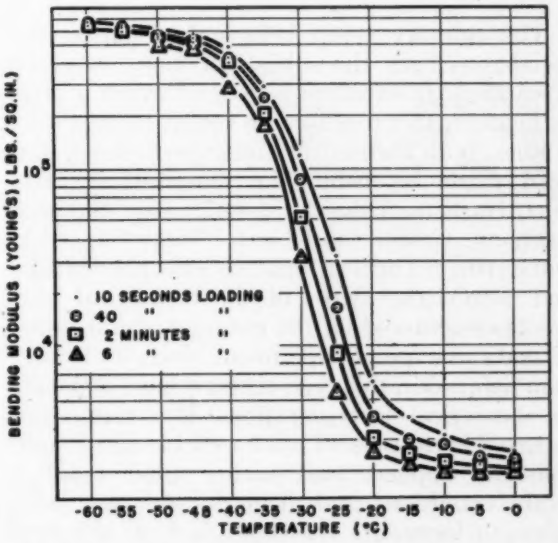

FIG. 12. Effect of loading time on Young's modulus of *B/A* type 3 stock containing no softener.

method of polymerization or a variation in the amount of controlling agent present. It is reasonable to expect that the modulus of an elastomer would depend on the molecular structure of the material. Hence, though the data are not sufficient to be conclusive, it is suggested that studies of this type might be useful in following

TABLE V. Stock formulae and brittle point temperatures. Thiokol FA, mass and emulsion polymerized polybutadiene, Hevea rubber compounds.

Stock designation	*A*	*B*	*C*	*D*	*E*	*F*	*G*	*H*
Pigment								
Hevea rubber	100	100						
Thiokol FA			100	100				
Emulsion polymerized butadiene					100	100		
Mass polymerized butadiene							100	100
Sulphur	3	3			2	2	2	2
Zinc oxide	3	3	10	10	5	5	5	5
Stearic acid	0.5	3.5	0.5	0.5	0.5	3	0.5	3
Mercaptobenzothiazole	1.0	1.0			1.5	1.5	1.5	1.5
Benzothiazyl disulfide			0.3	0.3				
Di-phenyl-guanidine			0.1	0.1				
Pine tar		3.0						
Bardol						5		5
Phenyl-beta-naphthylamine	1.0	1.0						
SRF black				40				
HPC black		50				50		50
"Optimum" cure	75′ @ 270°F	75′ @ 270°F	40′ @ 298°F	40′ @ 298°F	100′ @ 270°F	100′ @ 270°F	100′ @ 270°F	100′ @ 270°F
Brittle point temperature (°C)	−53	−53	−43	−37	<−74	<−74	−40	−41

changes in molecular structure as a function of the various steps involved in the polymerization process.

PRIMARY CREEP AT LOW TEMPERATURES

The primary creep behavior of plastic materials has been the subject of many extensive researches, an excellent survey of which is given in Leaderman's treatise.[2] In recent years similar studies, both theoretical and experimental, have been made on rubberlike materials by Hulburt, Harman, Tobolsky, and Eyring,[6] Simha,[7,8] Anthony, Caston, and Guth,[9] Eley,[10] Tobolsky and Eyring,[11] Tuckett,[12] and Kobeko, Kuvshinsky, and Gurevitch.[5] Most of the theoretical work has been centered on the constant strain (stress relaxation) type of experiment since, as Leaderman points out, this type of test is most amenable to theoretical interpretation. The creep data reported in the present work were obtained under constant applied load rather than constant strain conditions and attempts are now being made to formulate theories based on this type of test. One of the results of this study has been the establishment of a creep constant, based on experimentally determined quantities, which can be employed as a convenient index of low temperature serviceability of a compound.

At temperatures around 30°C, the ten-second modulus discussed above approaches the so-called total modulus. At low temperatures, i.e., under conditions such that primary creep takes place very slowly, the ten-second modulus is nearly identical with the instantaneous or (according to Kobeko) the acoustic modulus. At intermediate temperatures, the measured ten-second modulus depends, in varying degree, on both total and instantaneous moduli. According to the rather meager experimental data available, both total and instantaneous moduli are very nearly independent of temperature.[5] The results of some tests on a *B/A* type 3 stock

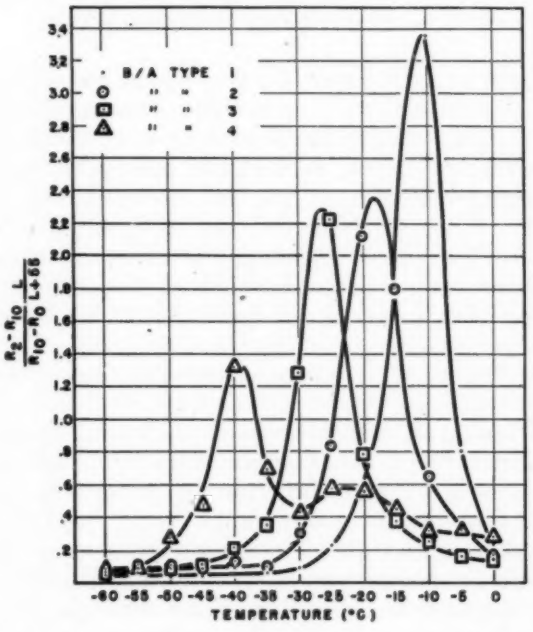

FIG. 13. Creep constants of *B/A* type stocks, containing no softener, as a function of temperature.

(containing no softener), shown in Fig. 12, confirm these conclusions. In this test, the Young's moduli at several loading times were measured as a function of temperature. At 0°C, most of the ultimate deflection including primary creep had taken place even before the ten-second measurement was taken. Consequently there is little difference between the ten-second and six-minute moduli, i.e., both approach the total modulus which in turn appears to be approaching a steady value at a temperature close to 0°C. At −60°C, only the instantaneous deflection and very little primary creep had taken place even after six minutes' loading. Hence very little difference in the moduli measured at the various loading times is again indicated. At intermediate temperatures the deflection measured at the ten-second loading time, for instance, includes only a part of the primary creep. Part of this creep takes place in the interval ten seconds to six minutes. Consequently, the two moduli are found to be considerably different.

It is this intermediate temperature, at which the ten-second modulus begins to depend on, or approach, the instantaneous modulus (as the temperature of the sample is lowered) which can be employed as a serviceability index. At temperatures well above this point, the measured ten-second deflection includes the deflection corresponding to the instantaneous modulus, plus a considerable amount of the deflection resulting from primary creep. In other words, the material at these temperatures responds relatively quickly to impressed forces and consequently possesses usable, rubberlike properties. At temperatures below this point, primary creep takes place very slowly, the measured ten-second modulus is high, and hence the material exhibits the characteristics of stiff, plastic rather than those of rubberlike materials.

Following Leaderman's notation, the total deflection of a simple beam after being loaded for a time n can be written

$$D_n=\frac{FL}{E}\{1+C\psi(n)\}, \tag{1}$$

where F is a form factor, L is the total applied load, E is the instantaneous modulus, C is a constant, and $\psi(n)$ is the creep factor (a function of time).

Now for a simple beam of rectangular cross section,

$$E=\frac{Ll^3}{4wt^3(\Delta R)}, \tag{2}$$

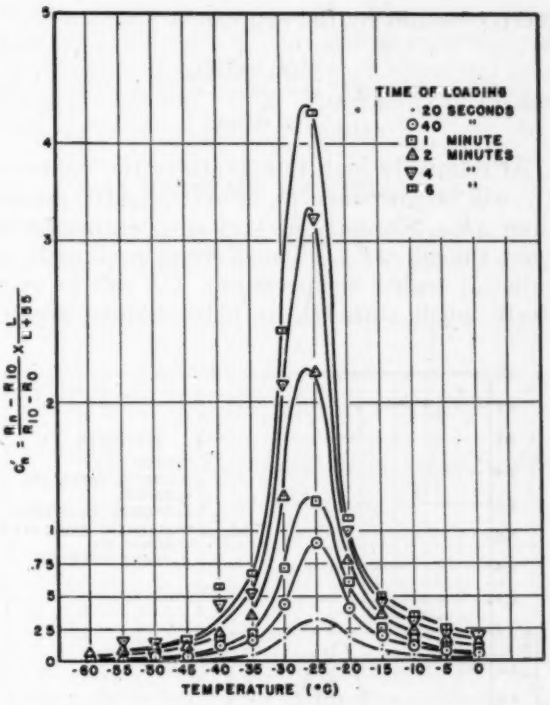

FIG. 14. Creep constants for B/A type 3 stock containing no softener, at various loading times, as a function of temperature.

where E is the instantaneous modulus, L is the total applied load as in (1) above, l is the distance between beam supports, w is the width of sample, t is the thickness of sample, and (ΔR) is the instantaneous deflection.

The form factor F, in this case, from (2) is given by

$$F=\frac{l^3}{4wt^3}; \tag{3}$$

hence

$$D_n=\Delta R\{1+C\psi(n)\}. \tag{4}$$

For any given time of loading, $C\psi(n)$ will be a constant which can be denoted by C_n. Hence from (4) above we obtain

$$C_n=\frac{D_n-(\Delta R)}{(\Delta R)}. \tag{5}$$

The term (ΔR) in Eq. (5) represents the instantaneous deflection which cannot be accurately determined experimentally except at very low temperatures. If the ten-second deflection be substituted in an equation of the form of (5) above, we can define a modified, or experimental,

creep constant by the expression

$$C_n' = \frac{D_n - \Delta R_{10}}{\Delta R_{10}}. \quad (6)$$

At relatively high temperatures the values of C_n' will be low since D_n is only slightly greater than ΔR_{10}. Similarly at very low temperatures, even though ΔR_{10} is small compared with its value at higher temperatures, C_n' will be relatively small since D_n is only slightly greater

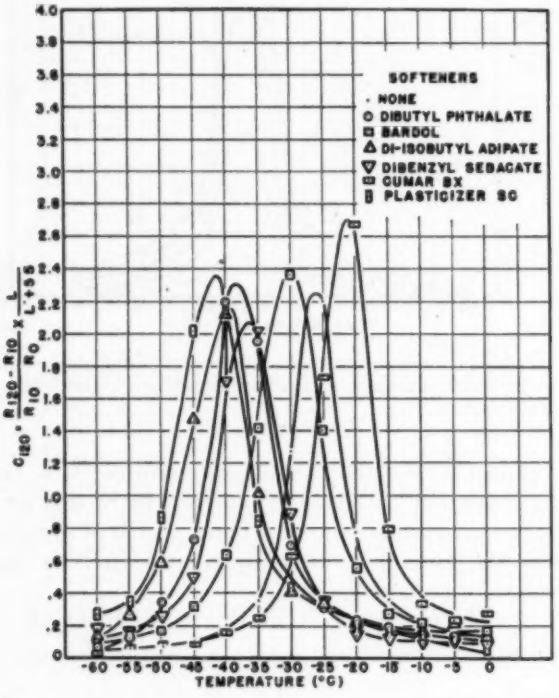

FIG. 15. Creep constants for B/A type 3 stocks as a function of temperature.

than ΔR_{10}. At some intermediate temperature, where D_n is significantly greater than ΔR_{10} (i.e., a large part of the primary creep takes place in the time interval ten to n seconds), the value of C_n' will reach a maximum. In the region of the temperature at which this maximum in the experimental creep constant occurs, the ten-second deflection under a given applied stress decreases rapidly, with decrease in temperature. In addition, primary creep rate is reduced sharply so that the character of the material changes from a soft, rubberlike substance which is easily and quickly deformed by stress application to a hard, (and sometimes brittle) substance which is deformed with difficulty.

By definition,

$$D_n = R_n - R_0, \quad (7)$$

and

$$(\Delta R_{10}) = R_{10} - R_0, \quad (8)$$

where R_n and R_{10} are the dial gauge readings at a time n and 10 seconds, respectively, and R_0 is the "zero" load dial gauge reading obtained in the manner previously described. Hence from (6), (7), and (8), we may write

$$C_n' = \frac{R_n - R_{10}}{R_{10} - R_0}. \quad (9)$$

The above expression presumes the load corresponding to R_0 to be zero. In fact, even with the counterbalanced system the initial load is 55 grams. At the higher temperatures, the load added to obtain R_{10} may in some instances be of the same magnitude as the initial load. The difference between R_{10} and R_0 as experimentally determined on the present apparatus is hence smaller than it should be by the ratio of the loads employed in the two cases (assuming Hooke's law to hold as a first approximation). The denominator in (9) above should hence be written

$$(R_{10} - R_0) \times \frac{L+55}{L}. \quad (10)$$

The numerator requires no such correction, since both R_n and R_{10} are measured with the total load applied. The experimental creep constants measured and plotted as a function of temperature were thus calculated from the final expression

$$C_n' = \frac{R_n - R_{10}}{R_{10} - R_0} \times \frac{L}{L+55}. \quad (11)$$

Experimental creep constants have been determined for the same series of B/A type stocks described earlier. The results are shown in Fig. 13 for the stocks containing no softeners. The temperatures at which the maximum creep constant occurs are given in Table VI together with the temperatures at which the moduli of the same stocks reached a value of 10^4 lb./sq. in. It can be seen that a reasonably constant difference in temperature exists between the two indices, except for the B/A type 4 stock, which exhibits a small, secondary maximum at a relatively high temperature.

The data shown in Fig. 13 were calculated from ten- and 120-second deflection readings. Creep

TABLE VI. Critical temperatures (°C) for B/A type stocks containing no softeners.

Copolymer type	1	2	3	4
@ Modulus 10^4 lb./sq. in.	−6	−11	−22	−28
@ Maximum creep constant	−11	−18	−26	−39

constants were also calculated for one of the stocks (B/A type 3, no softener) for several different time intervals. These data, shown in Fig. 14, illustrate the reproducibility and accuracy obtainable by this experimental method and analysis.

The effect of some softeners on the creep constants of one of the stocks is shown in Fig. 15. The temperatures at maximum creep constant and at a modulus of 10^4 lb./sq. in. are given in Table VII. As in the instance above, the differences in the two sets of temperatures are quite constant, the maximum creep constant temperatures again being somewhat lower than those derived from the 10^4 lb./sq. in. modulus values.

Creep factors having greater theoretical importance than the creep constants discussed earlier can also be calculated from the data obtained if Kobeko's hypothesis (that the instantaneous modulus is independent of temperature) is accepted. If, in (1) above, we write

$$C\psi(n) = C_n, \tag{12}$$

for any given time of loading, we obtain

$$C_n = \frac{D_n E}{FL} - 1. \tag{13}$$

If we assign to E in the above expression the value calculated from deflection observations made at extremely low temperatures, then creep factors can be calculated from the observed total deflections D_n. Typical data obtained in two B/A type 3 stocks and calculated by this method are shown in Fig. 16, for a 120-second loading period. Although a definite difference between the two stocks tested is shown by this method of analysis, the possibility of employing these results in some way as a practical serviceability index is not readily apparent. Since, however, this analysis is based on more rigorous theoretical grounds than the experimental creep constant method,* these data should be of more interest to the theoretical analyst.

SUMMARY OF RESULTS

The low temperature Young's modulus of copolymers of the butadiene-acrylonitrile (B/A) type was found to be lowered by a reduction in the acrylonitrile content of the copolymer.

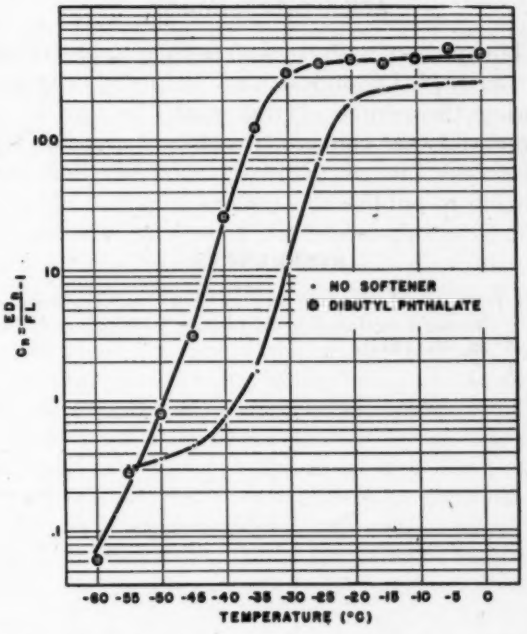

FIG. 16. Creep factors based on two-minute loading time using −60°C modulus value for E.

Mass and emulsion polymerized butadiene were found to possess considerably different low temperature physical characteristics.

Certain plasticizers (employed to improve low

* It should be noted, however, that in the final analysis, Kobeko's hypotheses are not based on molecular theory, but rather on experimental creep observations which lead to the concepts of instantaneous and total moduli. Phase changes resulting from temperature variation are also neglected in Kobeko's work.

TABLE VII. Critical temperatures (°C) for B/A type 3 stocks containing various softeners.

	No softener	Dibutyl phthalate	Bardol	Di-isobutyl adipate	Dibenzyl sebacate	Cumar BX	Plasticizer SC
@ Modulus 10^4 lb./sq. in.	−22	−34	−26	−38	−34	−19	−39
@ Maximum creep constant	−26	−38	−30	−41	−36	−21	−42

temperature properties) imparted a time-stiffening effect to compounds which, in the absence of the given plasticizer, showed no time effect.

An experimental method for the measurement of primary creep of elastomers at low temperatures is described. Calculation of a creep constant, as defined, appears to yield a critical temperature which may be useful as a serviceability index.

ACKNOWLEDGMENT

The authors wish to express their appreciation to Dr. J. H. Dillon for many helpful discussions during the course of this work, to Dr. J. N. Street for his continued interest, and to The Firestone Tire & Rubber Company for permission to publish this paper.

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Calendar of Meetings

November

11	American Physical Society, New York State Meeting, Schenectady, New York
14	Physics Club of Chicago, Chicago, Illinois
16–18	Electron Microscope Society, Chicago, Illinois
17–18	Society of Rheology, New York, New York

December

1– 2	American Physical Society, Chicago, Illinois
12	Physics Club of Chicago, Chicago, Illinois
16	American Physical Society, Pasadena, California

January

9	Physics Club of Chicago, Chicago, Illinois
19–20	American Physical Society, New York, New York
22–26	American Institute of Electrical Engineers, New York, New York

February

13	Physics Club of Chicago, Chicago, Illinois

March

13	Physics Club of Chicago, Chicago, Illinois

April

10	Physics Club of Chicago, Chicago, Illinois

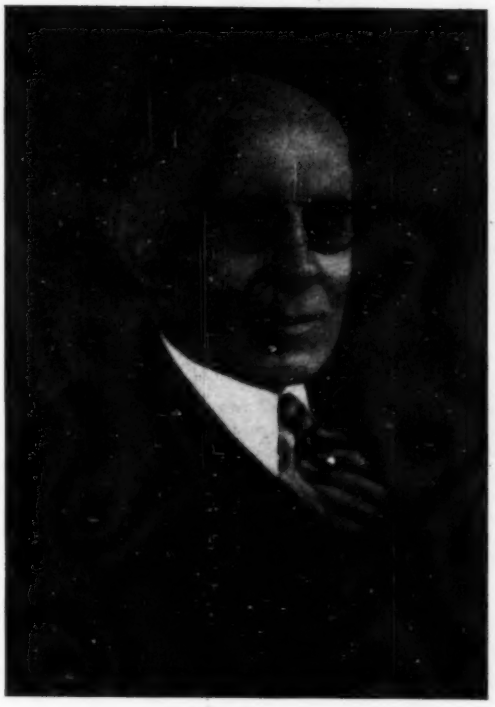
May

8	Physics Club of Chicago, Chicago, Illinois

June

25–29	American Institute of Electrical Engineers, Detroit, Michigan

The Frank B. Jewett Fellowships in the Physical Sciences



Frank Baldwin Jewett

IN honor of Dr. Frank B. Jewett, a pioneering proponent of the application to industry of the research methods of science, the American Telephone and Telegraph Company has inaugurated a series of fellowships.

The FRANK B. JEWETT FELLOWSHIPS are post-doctorate fellowships. They are intended to stimulate and to assist research in the fundamental physical sciences, and particularly to provide their holders with opportunities for individual growth and development as creative scientists. The fellowship awards will enable their recipients to devote themselves to research in pure science for a year or two following their doctorates.

The American Telephone and Telegraph Company has established a trust fund sufficient to finance five of these fellowships in each of the ten years, 1945–1954, inclusive. Five members of the staff of Bell Telephone Laboratories, Incorporated, will serve as trustees and award the fellowships.

The Frank B. Jewett Fellowships will be awarded on February first of each year. Each fellowship is for a term of one year, starting July first. An award may be extended by renewal to cover the succeeding year; but no individual shall receive awards for more than two terms.

Each fellowship carries an honorarium of $3000 payable in twelve equal monthly installments. Each fellow will be expected to make his own arrangements with the academic institution of his choice for facilities for his research. An honorarium of $1500 will be paid to the academic institution towards defraying the expense of the facilities it provides.

Since the purpose of the fellowships is to provide for the full-time continuation of academic research, awards will normally be made to those who have obtained the doctorate within the preceding year, or are expected to receive that degree not later than the beginning of the next fellowship term.

Awards of fellowships will be made by the trustees on recommendation of the Frank B. Jewett Fellowship Committee. The committee, appointed by the trustees, will consist of seven members of the scientific staff of Bell Telephone Laboratories who are actively and creatively engaged in research in the respective fields of physics, mathematics, and chemistry.

In the selection for fellowship awards the primary criteria will be: demonstrated research ability of the applicant, the fundamental importance of the problem he proposes to attack, and the likelihood of his growth as a scientist.

Selection for a fellowship award and its acceptance shall involve no implication or commitment on the part of the Bell Telephone Laboratories or on the part of the recipient as to later employment in the Laboratories.

Applications for fellowships should be directed to the Frank B. Jewett Fellowship Committee, Bell Telephone Laboratories, Inc., New York 14, New York. Applications should be received prior to December first preceding the term of the fellowship. Each application should contain biographical and scholastic data, a description of the research problem on which the applicant is at the time engaged, or has most recently completed, and an analysis of the problem in which he would expect to engage if appointed.

Here and There

Honors and Awards

During the 120th commencement exercises, Rensselaer Polytechnic Institute conferred the honorary degree of Doctor of Engineering upon Allen B. Du Mont, President of the Allen B. Du Mont Laboratories, Inc., of Passaic, New Jersey, and graduate of the Class of 1924. He was cited particularly as "a pioneer in the development and use of the cathode-ray tube, which today is the heart of the weapon, radar. He has also improved the science and art of television and promoted it in public consciousness through the ownership in New York City of one of the first television stations."

Staff Changes

With postwar planning in view, announcement of changes in the Engineering Department of the Weston Electrical Instrument Corporation, Newark, New Jersey, has been made by Caxton Brown, President of this company. John H. Miller, who has been Assistant Chief Electrical Engineer, has been promoted to Chief Electrical Engineer. Frank X. Lamb has been made Assistant Chief Electrical Engineer. He formerly was a project engineer. Karl M. Lederer, formerly Assistant Chief Engineer, is now Assistant Director of Research. W. N. Goodwin, Jr., continues as Vice President in charge of research and engineering. He relinquishes his post as Chief Engineer, but retains his present title of Director of Research. He also will be available for consultation and guidance in engineering matters in general.

Physics Club of Chicago

The Physics Club of Chicago has announced the following officers for 1944–45: *President*, B. J. Barmack: Senior Engineer, Equipment and Research Section, Engineering Department, Commonwealth Edison Company. *Vice President*, Mark Ered: Metallurgical Laboratory, University of Chicago. *Treasurer*, Louis Robertson: Patent Attorney, Mann, Brown and Cox. *Secretary*, William F. Einbecker: Head of the Science Department, Highland Park High School. *Directors*, Arni Helgason: Vice President, Essex Wire Corporation, and General Manager, Chicago Transformer Division; Eugene W. Skinner: Professor of Physics, Northwestern University Dental School; and M. N. States: Director of Research, Central Scientific Company.

The meetings of the Physics Club of Chicago are held regularly on the second Tuesday of each month, October through May, at 7:00 P.M., Chicago Lighting Institute, Commonwealth Edison Building, 72 West Adams Street, Chicago, Illinois.

Necrology

Edward Bausch, Chairman of the Board of the Bausch & Lomb Optical Company, died at the age of 89 in his home in Rochester, New York, July 30, 1944. A son of John Jacob Bausch, one of the founders of the company, he was initiated at an early age into the business which became his life work. At the age of 14, he evinced great skill with tools and showed an aptitude for optical design. This was borne out later in the first microscope he designed and built in 1872.

Beginning in 1883, his activity in the development of the microscope and other laboratory instruments was evident in a succession of patents. Trichnoscopes, illuminators, microtomes, invertible microscopes, binocular microscopes, and centrifugal testing machines were followed in 1887 by his famous iris diaphragm shutter which made the snapshot camera a popular plaything. In the latter part of the 19th century, the United States Navy, seeking a domestic source of supply for searchlight mirrors, turned to Edward Bausch and his organization. He substituted parabolic curves on these mirrors for the old Mangin type and developed a new silvering process to withstand the heat. During this same period he worked in close collaboration with George N. Saegmuller, Chief of the Instrument Division of the U. S. Coast Survey, furnishing the optics for many of Saegmuller's designs. Optical requirements brought him to Rochester with increasing frequency and in 1905, he joined Bausch & Lomb. Since then, Edward Bausch and his associates have collaborated closely with the armed forces of the United States in the development of military instruments and with the outbreak of World War I were successful in meeting one of the most critical emergencies facing the country, the production of optical glass.

Dr. Bausch was active in the planning and the expansion of the company for the present war until a year ago when illness curtailed his visits to the plant, but he followed the progress of the company through the personal reports delivered to his home by company executives.

War Surplus Optical Supplies

War surplus optical items are now being placed on the market. Various types of tank prisms, roof prisms, achromatic lens combinations, porro-Abbe prisms, and lenses of various types are being made available. These are likely to be of special interest to colleges and research laboratories. Further information concerning available items may be obtained from the Edmund Salvage Company, 27 West Clinton Avenue, Oaklyn-Audubon, New Jersey.

Hunter College Alumnae

Miss Ruth Lewinson, President of the Associate Alumnae of Hunter College, has announced that she would like to have all women physicists who are graduates of the college contact her at 18 East 41 Street, New York 17, New York. Hunter College is about to celebrate its 75th birthday and is eager to have as many of its graduates as possible participate in that occasion.

Research Conference on X-Ray and Electron Diffraction

The University of Pittsburgh scheduled the first of a series of annual research conferences on x-ray and electron diffraction on Friday and Saturday, November 3 and 4. The program included a series of papers contributed mainly by men from the University of Pittsburgh, Carnegie Institute of Technology, and from the x-ray and electron diffraction laboratories of industries in the Pittsburgh area.

The Friday afternoon session was concerned with x-ray diffraction investigations on wheat flour gluten, electrolytically deposited silver on cold-rolled metals, anhydrous iron-alkali sulfates, coloring agents in mottled silica brick, sodium bicarbonate–sodium carbonate conversion, and tungsten-molybdenum alloys. Friday evening there were scheduled invited papers covering x-ray diffraction studies on materials of physical and metallurgical interest by Professor W. P. Davey of The Pennsylvania State College, and on materials of biological interest by Professor I. Fankuchen of Polytechnic Institute of Brooklyn.

The theory and application of electron diffraction, chemical and metallurgical analyses by electron microscopy, the use of electron microscopy in confirming indirect methods for determining dimensions of colloidal particles, and special techniques in x-ray diffraction were included in a session on Saturday morning. Participants in the conference were invited to inspect the x-ray diffraction laboratories of the district on Saturday afternoon. All sessions were held in the auditorium of the Mellon Institute.

Contributed Original Research

Stress-Temperature Relations in a Pure-Gum Vulcanizate of Natural Rubber*

LAWRENCE A. WOOD AND FRANK L. ROTH
National Bureau of Standards, Washington, D. C.

(Received July 17, 1944)

Stress-temperature relations at constant elongation have been studied in a pure-gum vulcanizate of natural rubber. Such studies yield information useful for calculations involved in the theory of its elastic behavior, and furnish practical data regarding its tensile properties at different temperatures. The crystallization of the rubber which occurs on stretching is a factor of considerable importance in the explanation of the results obtained. The compound contained 100 parts by weight of smoked sheet rubber, 2 parts of sulfur, 1 part of zinc oxide, and 0.5 part of zinc dibutyl dithiocarbamate ("Butyl zimate"), and it was vulcanized 40 minutes at 115°C. The stress-temperature studies were made after the specimens were stretched and allowed to relax at a constant temperature of 25°C or 70°C for about two hours. The change of stress with time at the end of two hours was small enough to be without influence on later results, except when the flow was excessive or when the stretched rubber continued to crystallize, as it did at elongations between 150 percent and 500 percent at 25°C. At elongations of 150 percent and less, no evidences whatever of crystallization were found during the time of the experiments. At elongations of 500 percent and more, the crystallization which occurred during stretching and in the first few minutes thereafter was so complete that the stress soon became independent of time. At 70°C both the upper and lower limits of the range of elongations in which continued crystallization occurred were somewhat higher. Values of the stress after relaxation have been used to plot a stress-strain curve. The stress-temperature relations obtained by lowering the temperature to about −20°C were always linear and reproducible on successive runs of increasing and decreasing temperature, except when the flow was excessive or when the stretched rubber continued to crystallize. An additional period of relaxation was required if the rubber was heated above the temperature at which the first relaxation occurred. The slopes of the stress-temperature lines and the values of the stress at any temperature depend upon the temperature at which relaxation was carried out. The stress intercepts at 0°K are small compared with the total stress for elongations up to 150 percent. At the higher elongations the intercepts take on increasingly large negative values, finally becoming approximately equal in magnitude to the total stress.

I. INTRODUCTION

THE stress-temperature relations found in natural rubber are of considerable importance in understanding its elastic behavior. Studying stress as a function of temperature makes it possible to conduct experiments in such a way that there is a minimum amount of relative movement of the different portions of the rubber during the course of the observations. The results of studies made in this way are less influenced by effects arising from friction and flow than are those in which there is relative movement.

In the course of the present investigation the stress-temperature relations for a pure-gum vulcanizate of natural rubber were investigated under conditions of constant elongation. The upper limit of elongations was set by the breaking of the specimen between 700 and 800 percent. The limits of temperature were from 70°C to about −10°C. As incidental parts of the investigation the following results were obtained: (1) intercepts for the stress-temperature relations at 0°K; (2) stress relaxation in the rubber during the first few hours after stretching; and (3) stress-strain relations after such relaxation. The stress-strain relations may be considered as approaching equilibrium values for elongations up to about 150 percent, since nearly the same values are obtained following extension or retraction.

The crystallization of the rubber which occurs on stretching and which may continue to increase after stretching has been found to be a factor of very considerable importance in the explanation of the results obtained. In the particular compound studied no effects ascribable to crystallization were observed at 25°C at elongations below 150 percent. At elongations above 500 percent the crystallization which occurs during stretching and in the first few minutes thereafter is apparently so complete that no later changes as-

* Presented on November 13, 1943 before the Symposium on the Physics of Rubber and Other High Polymers held by the American Physical Society at Evanston, Illinois.

sociated with continued crystallization are noted. At elongations between 150 percent and 500 percent crystallization continues for hours after stretching.

II. EXPERIMENTAL PROCEDURE

1. Compound and Specimens

The compound studied was as follows:

	Parts by weight
Smoked sheet natural rubber	100
Sulfur	2
Zinc oxide	1
Zinc dibutyl dithiocarbamate (butyl zimate)	0.5
Total weight of compound	103.5.

It was vulcanized for 40 minutes at 10 lb./in.^{2} steam pressure. The time selected was that which gave a vulcanizate of maximum stiffness. This particular compound was chosen because it seems to involve the addition of about a minimum quantity of compounding ingredients to the raw rubber to produce a well-vulcanized product. The addition of an anti-oxidant in the compound would have produced a vulcanizate which would have remained somewhat more stable for long periods of storage and would have been subject to somewhat less flow at high temperatures.

The rubber specimens were flat dumbbells or strips measuring from 2 to 20 cm between gauge marks. They were stretched by dead-weight loading with manual control of the elongation, which could be observed by means of displaceable fiducial marks and a graduated scale viewed through a glass window.

The specimens, fiducial marks, and scale were contained in an enclosure through which a vigorous current of air was circulated by a blower. The air was heated by resistance coils of the type used in radiant heaters, or cooled by the use of dry ice. Consequently at the lower temperatures the specimens were surrounded by an atmosphere containing large amounts of carbon dioxide. No effects ascribable to the carbon dioxide could be noted.

2. Thermal Expansion

The distance between the gauge marks on the unloaded specimens was measured over the whole range of temperatures studied so that all elongations could be referred to the corresponding unstretched lengths at each temperature. There was moderately good agreement between the measured lengths and those calculated by the use of the linear expansivity 220×10^{-6} per degree C commonly employed in this laboratory for pure-gum vulcanizates.[1,2]

Throughout the present work the percentage elongation was always measured with reference to the unstretched length at that particular temperature, and not with reference to the unstretched length at room temperature or some other fixed temperature. In other words, as the temperature was varied the distance between gauge marks was not held constant but was kept proportional to the unstretched length at each temperature. Consequently the elongation, as just defined, was maintained constant as the temperature was varied.

The stress is defined for the purposes of the present work, in accordance with the usual practice, as the force per unit area of original cross section, the area being measured at room temperature.

3. Relaxation of Stress

The specimens were stretched to the desired elongation and first held at a constant temperature of 25°C or 70°C for about two hours with periodic observations of the stress. On some occasions observations were extended over a period of six or eight hours.

4. Stress-Temperature Variations

After the relaxation of stress at constant temperature, the temperature was then lowered by steps. In order to maintain the elongation at a constant value it was found necessary to reduce the load. Next the temperature was usually raised while the load was again increased. In some cases the variation was repeated through a number of cycles always at constant elongation.

At the conclusion of the experiment the load was removed, and the specimen was heated to a temperature of 90–100°C in the unstressed state. It was then stored at room temperature for about 1 or 2 days. At the conclusion of this period the distance between gauge marks was measured with a magnifying glass and a steel scale graduated in hundredths of an inch. The increase in

[1] L. A. Wood, "Values of the physical constants of rubber," *Proc. Rubber Tech. Conference* (London, 1938), p. 933. Reprinted in Rubber Chem. Tech. **12**, 130 (1939).

[2] N. Bekkedahl and L. A. Wood, "Crystallization of vulcanized rubber," Ind. Eng. Chem. **33**, 381 (1941). Reprinted in Rubber Chem. Tech. **14**, 347 (1941).

this distance above that measured at the beginning of the experiment was expressed as a fraction of the initial distance and recorded as "permanent set."

III. RESULTS

1. Stress-Time Relations

The stress-time curves shown in Fig. 1 are typical of those obtained at elongations of 150

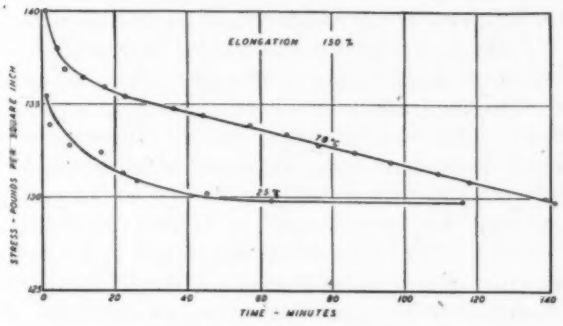


FIG. 1. Stress-time relations for an elongation of 150 percent at temperatures of 25°C and 70°C.

percent and less. The stress-time curves shown in Fig. 2 are typical of those obtained at elongations of more than 500 percent. The curves obtained at intermediate elongations show no approach to constant values of stress for times as long as six or eight hours. It is evident from Figs. 1 and 2 that at 70°C the stress shows no indication of approaching a constant value after two hours, but the curve becomes approximately a straight line. Such behavior was also observed at 25°C for elongations intermediate between 150 percent and 500 percent, but it is found to arise from a different cause, namely, crystallization, which will be discussed later. At 25°C outside this range of elongations, however, it is evident that the stress shows a definite approach to an equilibrium value or a quasi-equilibrium value. The exactness of approach to equilibrium at 25° was not investigated at longer times, since the only aim was to have no appreciable further change during the one or two hours, at the most, which might be required for observations of the stress-temperature relation. This condition was satisfied with sufficient exactness, under the conditions mentioned, by a relaxation period of not more than two hours. Under the conditions where a linear decrease of stress with time was observed, on the other hand, no approach to constancy was observed at the end of six or eight hours. It was thought that if the relaxation under either set of conditions were allowed to continue for periods of the order of days, oxidation phenomena and other extraneous effects might become noticeable and mask the short time effects under investigation.

2. Stress-Strain Relations

The stress-strain relations obtained after a 2-hour relaxation at 25°C are shown in the upper curves of Fig. 3. The same data at the lower elongations are plotted on an enlarged scale as the upper curves in Fig. 4. The numerical values are given in Tables I and II. The increase in stiffness

TABLE I. Experimental results on stress-temperature relations after relaxation at 25°C. Several days elapsed between vulcanization and testing.

Specimen number	Elongation Percent	Stress at 25°C lb.·in.$^{-2}$	Stress-temperature curve Slope lb.·in.$^{-2}$ ·deg.$^{-1}$	Intercept at 0°K lb.·in.$^{-2}$	Permanent set Percent
6	100	88.85	0.280	+5.4	0.15
5	200	136.3	0.467	−3	1.2
5	300	173.6	0.95	−109	1.2
4	400	201	1.88	−360	1.4
2	500	284	3.015	−614	2.4
1	600	624	4.6	−746	3
3	700	1257	7.85	−1093	6.3
9	780	2277	14.80	−2134	10.0

TABLE II. Experimental results on stress-temperature relations after relaxation at 25°C. Three months elapsed between vulcanization and testing.

Specimen number	Elongation Percent	Stress at 25°C lb.·in.$^{-2}$	Stress-temperature curve Slope lb.·in.$^{-2}$ ·deg.$^{-1}$	Intercept at 0°K lb.·in.$^{-2}$	Permanent set Percent
9*E*	10	19.6	0.0546	3.3	0.2
7*E*	20	34.5	0.1045	3.4	0.5
8*E*	50	68.0	0.223	0.7	0.2
8*E*	100	97.0	0.326	0.0	0.2
2*C*	150	130.0	0.452	−4.7	0.0
3*C*	200	154.0	0.646	−37.5	0.6
6*B*	300	195.5	0.964	−92	0.6
7*B*	400	230.0	2.2	−426	1.6
5*G*	400	231.0	2.61	−548	1.0
2*G*	500	402.0	3.73	−710	1.4
5*D*	600	661.0	5.52	−1084	1.2
4*D*	700	1798.0	12.9	−2048	6.7

of the rubber during an aging period of three months can be noted from the two curves in each figure. It is thought probable that this increase would have been smaller if the rubber compound had contained an anti-oxidant. The values at elongations between 150 percent and 500 percent are affected by a continuation of crystallization after stretching, and are less reproducible than

those outside this range because of variations in the completeness of crystallization.

3. Stress-Temperature Relations

Typical results of stress-temperature variations at elongations of 20 percent, 400 percent, and 700 percent are plotted in Figs. 5–8, respectively. Typical results over the whole range of elongations are shown in Fig. 9. The numerical values of

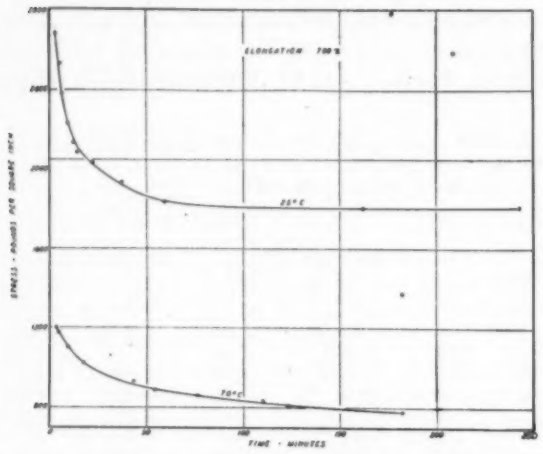


FIG. 2. Stress-time relations for an elongation of 700 percent at temperatures of 25°C and 70°C.

the slopes of these and a number of other stress-temperature graphs are given in Tables I–III.

TABLE III. Experimental results on stress-temperature relations after relaxation at 70°C. Three months elapsed between vulcanization and testing.

Specimen number	Elongation Percent	Stress at 70°C lb.·in.$^{-2}$	Stress-temperature curve Slope lb.·in.$^{-2}$ ·deg.$^{-1}$	Stress-temperature curve Intercept at 0°K lb.·in.$^{-2}$	Permanent set Percent
9*E*	10	20.6	0.058	0.4	0.2
7*E*	20	37	0.101	2.4	0.5
2*E*	50	67.5	0.187	3.4	1.5
5*E*	100	100	0.277	5.0	3.0
2*C*	150	130	0.350	9.3	3.3
1*G*	200	157	0.421	13.0	7.1
4*G*	300	224	0.783	−45.0	8.3
1*I*	300	247	0.985	−82	
3*F*	400	321	1.34[a]	−149[a]	
			2.30[b]	−468[b]	
7*G*	500	382	2.93	−632	8.5
10*D*	600	471	3.50	−732	6.3
3*D*	700	783	5.41	−1072	16.0

[a] Amorphous.
[b] Crystalline.

(*a*) *Relations at Low Elongations*

At elongations of 150 percent and less, typified by Fig. 5, a linear relation was always found between stress and temperature, and the same values of stress were obtained for increasing temperature as for decreasing temperature. This was approximately true even when the relaxation had been carried out at 70°C, as shown by the lower curve of Fig. 5.

Repeated cycles of variation of temperature produced the same values of stress. Within the limits of observation the stress was now found to be no longer a function of time, but to depend solely upon the elongation, the temperature, and the temperature at which relaxation had occurred.

If the temperature was raised above that at which relaxation had occurred, straight lines were not obtained, since further relaxation occurred at these higher temperatures, and the stress became again dependent upon the time. After relaxation the straight lines could be obtained as before by lowering the temperature. It can be noted from Fig. 5 that the value of the stress at a given temperature shows a strong dependence upon the temperature at which the relaxation occurred.

The same values were obtained after relaxation at 70°C regardless of whether or not relaxation at 25°C had occurred previously. However, the values after relaxation at 25°C were materially lowered by an immediately previous relaxation of the specimen at 70°C.

The values of the stress after a two-hour relaxation were of course found to be higher at the higher elongations, as were also the slopes of the straight lines representing the stress-temperature relation, as can be noted in Fig. 9.

(*b*) *Relations at High Elongations*

At elongations of 500 percent and more, typified by Fig. 8, the stress at any given temperature was again independent of time and was the same whether the temperature was increasing or decreasing. However, at 70°C this limit of elongation was considerably higher than 500 percent.

(*c*) *Relations at Intermediate Elongations*

At elongations intermediate between 150 percent and 500 percent at 25°C, the region in which the stress-time curves showed no approach to constancy, the stress-temperature relations were naturally much more complex than those outside this region. If after two hours of relaxation the temperature was lowered, the decrease of stress with time continued and often became more rapid. Consequently the stress-temperature relation was found to be time-dependent. If the

temperature changes were made sufficiently rapidly, straight lines could be obtained similar to those in Figs. 5 and 8, but the values of the stress at each temperature generally became lower as the experiment continued. A series of observations illustrating this behavior is represented by the data given in Fig. 6 and refers to sample 7*B* listed in Table II. The slope and intercept given in this table are those of the bisector of the angle between the two lowest lines shown in Fig. 6. The bisector was chosen rather than either line because it was thought that it would be less affected by the crystallization during the run. The table also lists results obtained with specimen 5*G* when, after a 20-hour relaxation, the temperature was lowered to −20°C. The values given are those of the slope and intercept of the line obtained as the temperature was raised from −20°C to +25°C.

At the conclusion of experiments of the type just described, the permanent set previously discussed was found to be small, and this behavior appears to be the result of a continuation of crystallization after stretching rather than any effects related to flow. Crystallization will be discussed in a later section.

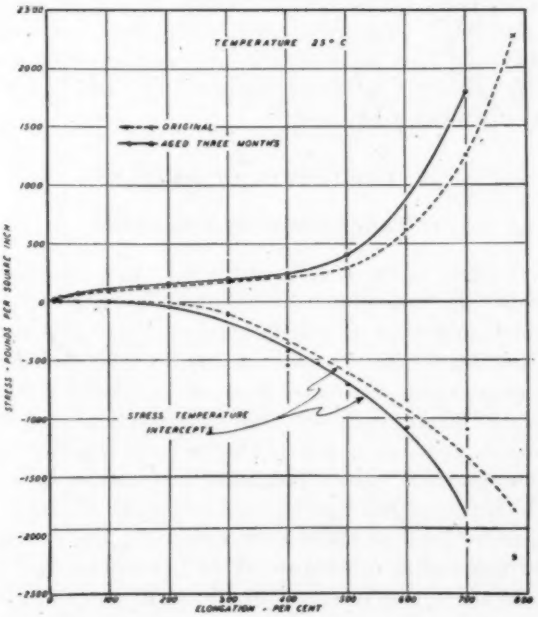


FIG. 3. Stress-elongation relations and intercepts of stress-temperature curves at 0°K. The specimens were relaxed at constant elongation for about 2 hours at 25°C. The broken-line curves were obtained from specimens which were cured from 4 to 8 days before testing. The specimens for the solid line curve were prepared about 3 months before the tests were made.

If the elongation is carefully selected, stress-temperature relations may be obtained showing crystallization effects which are small or negligible at the higher temperatures and quite pronounced at the lower temperatures, with subsequent melting as the temperature is raised. Thus the variations of stress resulting from the temperature variations indicated by arrows in Fig. 7 illustrate the transition between the two types of

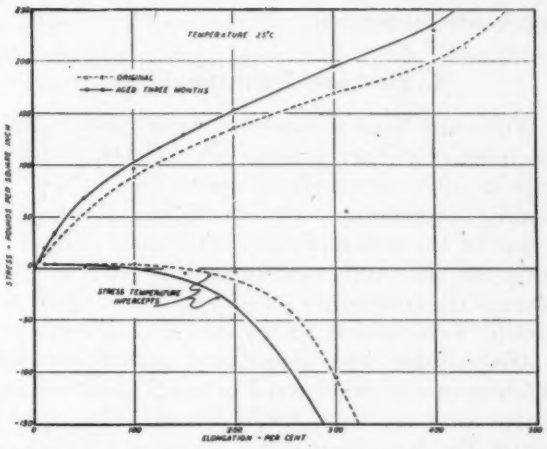


FIG. 4. Stress-elongation relations and intercepts of stress-temperature curves at 0°K. This figure is an enlarged portion of Fig. 3.

behavior at a fixed elongation. In this case it can be seen that the stress at 70°C at the end of the experiment was only about 3 or 4 percent below its original value. This may very well have been owing to a continuation of the relaxation of stress as shown in the 70° curves of Figs. 1 and 2.

4. Intercepts of Stress-Temperature Graphs

Stress-temperature graphs like those in Figs. 5–9 may be readily extrapolated analytically to find the values of the intercepts at 0°K. There is considerable theoretical interest in the values of such intercepts, when the relations are linear, as they are here, or in general in the intercepts of the tangents to such graphs in cases in which the relation is not linear.[3] The actual curve representing the behavior of the rubber at temperatures below those which were observed has no bearing on this linear extrapolation, of course. The values of the intercepts found at different elongations are plotted as the lower pairs of curves in Figs. 3 and

[3] K. H. Meyer, Chem. and Ind. **57**, 439 (1938). K. H. Meyer, *Natural and Synthetic High Polymers* (Interscience Publishers, Inc., New York, 1942), p. 154.

4. The numerical values are given in Tables I and II.

For a constant elongation equal to zero it follows that the load should always be zero. The corresponding stress-temperature graph coincides with the temperature axis, and its intercept, of course, is zero. If then the intercept approaches zero at zero elongation, the positive values found at low elongations would indicate that the intercept passes through a maximum at some elongation below 50 percent.

5. Flow and Permanent Set

When the load is removed from a stretched specimen of rubber it does not immediately retract to its exact original dimensions. There is usually a temporary set, which disappears in a period of the order of days at normal temperatures. If the rubber is heated or swollen by solvents the temporary set disappears much more rapidly. Treloar[4] has shown that even for unvulcanized rubber the amount of permanent set which cannot be removed is a much smaller part of the total set than had been previously suspected. The permanent set is, of course, a measure of the irreversible flow which has occurred.

In the present work values found for the permanent set are given in Tables I–III. When the permanent set was more than 2 percent of the original length, as was the case with almost all the measurements at 70°C, less reliance was placed on the results. When the permanent set was large at elongations other than those near the breaking point, the stress-time relations were like that shown for the relaxation at 70°C in Fig. 1 rather than like that shown for the relaxation at 25°C. At elongations near the breaking point the permanent set was always large. It will be noted that the compound used contained no anti-oxidant. If an anti-oxidant had been incorporated it is probable that the flow at 70°C would have been considerably less.

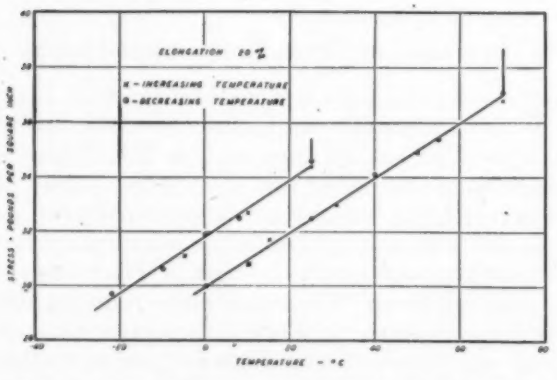


FIG. 5. Stress-temperature relations for an elongation of 20 percent. The vertical line at the point of highest temperature shows the amount of relaxation and the temperature at which it occurred.

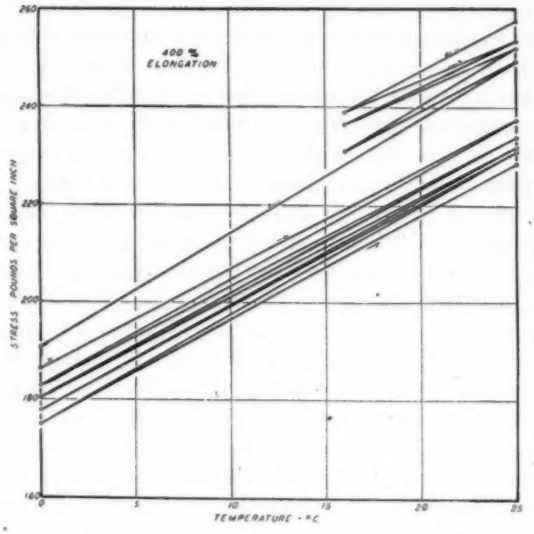


FIG. 6. Stress-temperature relations for an elongation of 400 percent. The specimen was allowed to relax about 2 hours at 25°C. About 2 hours more elapsed during complete cycle of events shown here.

IV. DISCUSSION OF RESULTS

1. Temperature of Relaxation

A study of the results obtained when the specimens were allowed to relax at 70°C leads to the conclusion that at all elongations there is a continued decrease of stress with time. This decrease appears to be caused by flow and is manifested by a large permanent set. For this particular compound, at least, less importance is to be attached to numerical values obtained in experiments in which relaxation was carried out at 70°C than in those relaxed at lower temperatures. The results obtained after relaxation at 25°C seem to be free from these objections, but the exact upper limit of satisfactory operation was not determined in this investigation. A dependence of the slopes and intercepts of the stress-temperature lines upon the temperature at which relaxation was carried out is evident from a comparison of Tables II and III.

[4] L. R. G. Treloar, "Elastic recovery and plastic flow in raw rubber," Trans. Faraday Soc. **36**, 538 (1940). Reprinted in Rubber Chem. Tech. **13**, 795 (1940).

The previous investigators of stress-temperature relations,[5–7] studying other rubber compounds, have allowed their specimens to relax only at temperatures of about 60° or 70°C. With the exception of a single graph for an unspecified temperature,[5] they have not presented any evidence regarding relaxation. A recently-completed investigation[8] has yielded much more complete information regarding relaxation at elevated temperatures, chiefly at 100°C and above.

2. Time of Relaxation

A study of the nature of the stress-time relation was not considered to be an aim of this investigation. Consequently no observations were made at very short time intervals after stretching, nor was the exactness of approach to a constant value investigated after a long time. A different experimental arrangement would have been set up if a more detailed study of relations of the types shown in Figs. 1 and 2 had been contemplated.

There is no doubt that the stress continues to decrease over periods of time much longer than those studied here. It is quite likely that such a decrease is associated with oxidation or with some other mechanism of a type not considered effective in observations extending over only a few hours.

Early studies of stress-time relations were made by Phillips[9] at a low elongation and by Schwartz[10] at an elongation of 100 percent. A recent investigation by Mooney and co-workers[11] included observations over a period of eight years.

3. Stress Relations in the Absence of Crystallization

Under conditions where crystallization does not occur, namely, at elongations up to 150 percent at 25°C in the present instance, the stress may be regarded as a quantity dependent upon the elongation, the temperature, the time, and the previous thermal and mechanical history of the specimen. A brief summary of the phenomena yielding the experimental results described in the preceding sections will serve to make the nature of the dependence clearer. The upper limit of temperature is taken as 25°C and the lower limit as about −20°C. The times considered will be of the order of hours rather than days so that effects of oxidation need not be considered. The theoretical basis of the phenomena is not considered in the present work.

At temperature T and elongation E there is a corresponding stress value S_E representing an equilibrium. The actual value S of the stress at a given time may not equal the equilibrium value S_E because of the lapse of insufficient time following some change in elongation or temperature. However, there is a closer and closer approach to S_E as time goes on. At 25°C the stress in the pure-gum vulcanizate studied attains a value within a few percent of S_E in one or two hours after the first application of a load. Thereafter there are no further changes with time, provided that the elongation is unaltered and provided that the temperature is not raised above that at which the relaxation occurred. No time effects are introduced by lowering the temperature and then raising it to the relaxation temperature or by repeating the variation a number of times. The

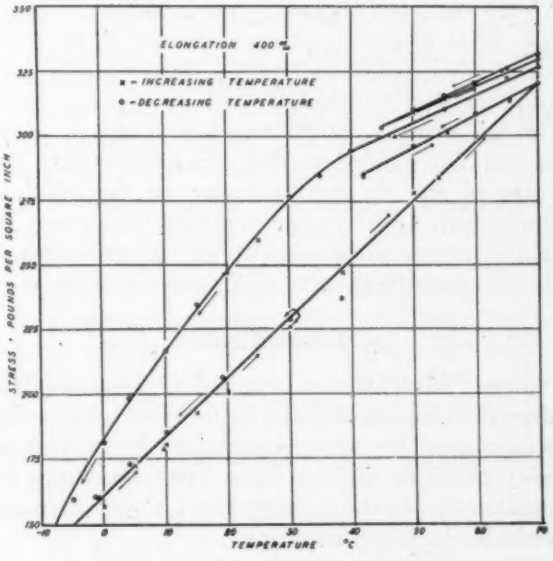


FIG. 7. Stress-temperature relations for an elongation of 400 percent after relaxation at 70°C.

[5] K. H. Meyer and C. Ferri, "The elasticity of rubber," Helv. Chim. Acta **18**, 570 (1935). Translated in Rubber Chem. Tech. **8**, 319 (1935).

[6] V. Hauk and W. Neumann, "The dependence of the stress on the temperature of rubber elongated to a constant degree," Zeits. f. physik. Chemie **A182**, 285 (1938). Translated in Rubber Chem. Tech. **12**, 520 (1939).

[7] R. L. Anthony, R. H. Caston, and E. Guth, "Equations of state for natural and synthetic rubberlike materials. I. Unaccelerated natural soft rubber," J. Phys. Chem. **46**, 826 (1942). Reprinted in Rubber Chem. Tech. **16**, 297 (1943).

[8] A. V. Tobolsky, I. B. Prettyman, and J. H. Dillon, J. App. Phys. **15**, 380 (1944).

[9] P. Phillips, Proc. Phys. Soc. London **19**, 491 (1905).

[10] A. Schwartz, J. Inst. Elec. Eng. **44**, 693 (1910).

[11] M. Mooney, W. E. Wostenholme, and D. S. Villars, J. App. Phys. **15**, 324 (1944).

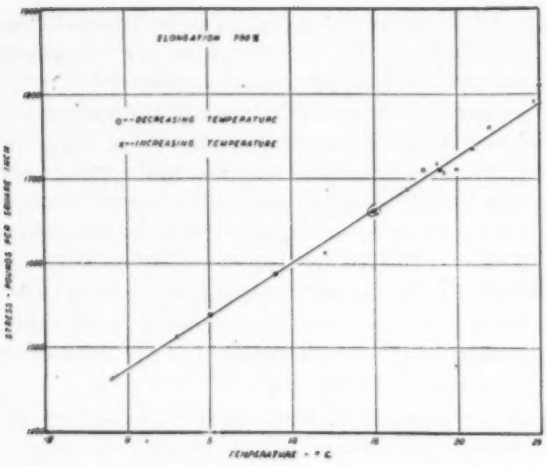


FIG. 8. Stress-temperature relations for an elongation of 700 percent.

stress-temperature relation under these conditions is linear.

A previous heating of the unstretched rubber which does not lead to oxidation appears to have no influence, but the stress is found to be temporarily less than S_E if the specimen has been heated to a temperature higher than T while stretched, or if it has been stretched to an elongation greater than E. Since time is required for the approach to S_E, it is clear that immediately after any stretching for the first time S will be greater than S_E. Immediately after any amount of retraction from a condition in which S has approached an equilibrium value, S will be less than S_E. The increase of S with time following a reduction of elongation and its approach to S_E from lower values was observed by Meyer and Ferri,[5] and has been confirmed by direct experiment in our laboratories. If the load is completely removed S is reduced to zero, which is less than the value of the S_E corresponding to the residual elongation. In time the residual elongation or temporary set disappears almost completely and the corresponding value of S_E approaches zero.

4. Crystallization

The crystallization of rubber on stretching has often been mentioned as a factor of importance in determining its elastic behavior. Nevertheless, most previous writers have been unwilling or unable to make the definite correlations which are desirable in this connection.

Three distinct regions in the stress-strain curve of rubber were recognized as early as 1910 when Schwartz[10] named them stage 1, stage 2, and stage 3. Wiegand and Snyder[12] discussed the regions in considerable detail under the designations region A, region B, and region C. A similar division was made by Williams and Sturgis[13] a few years later. Wiegand and Snyder were rather cautious about ascribing the effects to definite crystallization and preferred to speak merely of "profound structural changes." The other writers made no attempt whatever to explain the effects observed.

These regions appear well defined in the results of the present work. In region A, which extends up to an elongation of about 150 percent in the present compound at 25°C, we may say that there is no crystallization on stretching, or at any other time during the experiment. In region B, which includes elongations from about 150 percent to 500 percent, the crystallization which occurs on stretching is partial, and additional crystallization continues for a considerable time. In region C, at elongations greater than 500 percent, the crystallization which occurs on stretching and possibly during relaxation is so nearly complete that no further crystallization could be observed during the entire period of observation. A lowering of the temperature does not lead to any additional crystallization, nor does a return to the temperature at which the rubber was stretched give rise to melting.

Relaxation and the other stress relations discussed in the preceding section as characteristic of region A are also present in region B with a superposition upon them of the additional complexities associated with continuing crystallization. The simpler stress relations are again evident in region C.

The decrease of stress with continuing crystallization in region B has been noted previously.[5] In fact, working with unvulcanized rubber at −25°C and 0°C, Smith and Saylor[14] have found that crystallization can continue to such an extent that the stress not only decreases to zero

[12] W. B. Wiegand and J. W. Snyder, "The rubber pendulum, the Joule effect, and the dynamic stress-strain curve," Trans. Inst. Rubber Ind. **10**, 234 (1934). Reprinted in Rubber Chem. Tech. **8**, 151 (1935).

[13] I. Williams and B. M. Sturgis, "Composite nature of the stress-strain curve of rubber," Ind. Eng. Chem. **31**, 1303 (1939). Reprinted in Rubber Chem. Tech. **13**, 74 (1940).

[14] W. H. Smith and C. P. Saylor, "Optical and dimensional changes which accompany the freezing and melting of Hevea rubber," J. Research Nat. Bur. Stand. **21**, 257 (1938), RP 1129. Reprinted in Rubber Chem. Tech. **12**, 18 (1939).

but even becomes negative. If the distance between the ends of the specimen is held fixed, the specimen becomes bowed at the center. This effect was found to be small or negligible in region *C*.

Crystallization in stretched rubber has been investigated by previous workers using x-rays,[15] volume changes,[16] and double refraction.[17] It appears from the present work that stress-time or stress-temperature relations may also be used to locate the regions of elongation and temperature in which crystallization occurs and to gain additional information about its nature.

5. Application of Thermodynamics to Stress-Temperature Data

The results of studies of this kind may be used to evaluate the entropy and energy terms appearing in equations describing the elastic behavior of rubber. In fact, most of the previous observers[5, 7, 12] in this field have applied thermodynamic equations of the types discussed by Gerke[18] to their experimental data. The scope of the present paper does not permit such an application, with the necessary qualifications. This paper aims, rather, to describe and present at least some of the necessary experimental results.

It might be pointed out once again that the experiments described in the present paper were carried out at constant elongation. In this manner the data did not require the corrections for thermal expansivity applied by previous observers[5, 7] who observed stress-temperature relations at constant length and calculated from them stress-temperature relations at constant elongation. However, since the present work was initiated, theoretical interest, as exemplified in the work of James and Guth,[19] seems to be more concerned with stress-temperature relations at constant length than was previously the case. Relatively simple relations can be derived by which the stress-temperature relations at constant length can be obtained from the results presented here. The intercept of each stress-temperature relation at constant length is greater than that at constant elongation, while the slope is less. An experimental study of these relations is in progress.

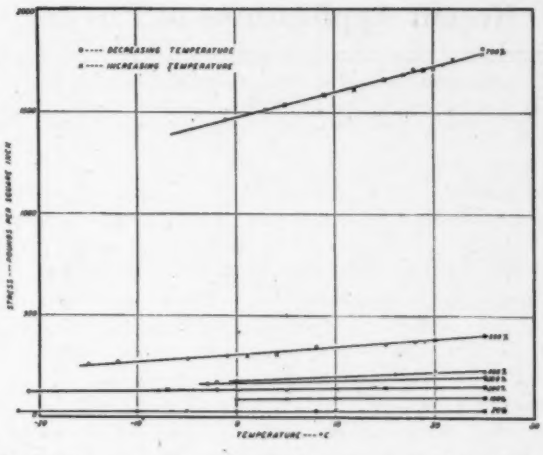


FIG. 9. Stress-temperature relations for various elongations.

V. SUMMARY

Stress-temperature relations at constant elongation have been investigated for a pure-gum vulcanizate of natural rubber. The rubber was first allowed to relax for about two hours at constant elongation and constant temperature in order to minimize the effects of short time relaxation of stress. The stress, except under special conditions, was changing very little at the end of this time. The stress-temperature relations for temperatures below the relaxation temperature could be represented by straight lines. The values of the slopes and intercepts of these lines are presented in tabular form. The stresses at the end of the relaxations were used as the basis of stress-strain curves. Crystallization was found to be an easily-recognized factor of considerable importance in the interpretation of the results.

[15] S. D. Gehman, Chem. Rev. **26**, 203 (1940).

[16] W. L. Holt and A. T. McPherson, "Change of volume of rubber on stretching; effects of time, elongation, and temperature," J. Research Nat. Bur. Stand. **17**, 657 (1936). Reprinted in Rubber Chem. Tech. **10**, 412 (1937).

[17] P. A. Thiessen and W. Wittstadt, "Forced and spontaneous changes in the arrangement of the molecules in stretched rubber. Crystals and fused phase in stretched rubber," Zeits. f. physik. Chemie **B41**, 33 (1938). Translated in Rubber Chem. Tech. **12**, 736 (1939).

[18] R. H. Gerke, "Thermodynamics of stressed vulcanized rubber," Ind. Eng. Chem. **22**, 73 (1930). Reprinted in Rubber Chem. Tech. **3**, 304 (1930).

[19] H. M. James and E. Guth, J. Chem. Phys. **11**, 455 (1943).